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A JOURNAL OF EXPERIMENTAL AND THEORETICAL PHYSICS

CONDUCTED
WITH THE CO-OPERATION OF THE

AMERICAN PHYSICAL SOCIETY

BY

EDWARD L. NICHOLS,
ERNEST MERRITT, and FREDERICK BEDELL

CLXXIV

NOVEMBER, 1910

A New Method of Determining the Optical Constants of Metals, and the Optical Constants of Silicon. L. R. INGERSOLL and J. T. LITTLETON, Jr. 489
Studies in Luminescence. XIV. Further Experiments on Fluorescence Absorption. EDW. L. NICHOLS and ERNEST MERRITT 500
A Noteworthy Interrelation of Illuminating Power, Density, and Viscosity of Certain Kerosene Oils. G. W. STEWART 513
Some Electrical Properties of Selenium. III. The Influence of Temperature upon the Recovery. LOUISE S. McDOWELL 524
On the Initial Velocity of Electrons as a Function of the Wave-Length in the Photoelectric Effect. JACOB KUNZ 536
Some Calorimetric Methods. WALTER P. WHITE 545
Lag Effects and Other Errors in Calorimetry. WALTER P. WHITE 562
The Molecular and the Frictional Flow of Gases in Tubes. Discussion by MARTIN KNUDSEN and WILLARD J. FISHER 586
On the Definition of a Perfect Gas. Remarks on the Paper of A. G. Webster and M. A. Rosanoff. G. BAKKER 589
The Grating Interferometer. C. BARUS and M. BARUS 591
Proceedings of the American Physical Society 599

Minutes of the Fifty-Third Meeting; A New Method of Measurement of Small Angles, *C. W. Chamberlain*; Note on "Changes in Density of the Ether and Some Optical Effects of Changes in Ether Density," *Charles F. Brush*; Preliminary Report on Temperature Coefficient of Resistivity of Copper, *J. H. Dellinger*; Certain Peculiarities of the Discrepancies Among Recent Wave-Length Determinations, *Irving G. Priest*; Discharge from Hot CaO, *C. D. Child*; The Freezing of Water Under High Pressure, *P. W. Bridgman*; The Action of Mercury on Steel at High Pressures, *P. W. Bridgman*; The Limit of Visibility in the Red, *Henry Phelps Gage*; Torsional Rotatory Polarization, *A. W. Ewell*; The Positive Thermions Emitted by the Salts of the Alkali Metals, *O. W. Richardson*; Gravitation and the Electron Theory, *O. W. Richardson*; The Scientific Results of the First Cruise of the "Carnegie" in Magnetism, Electricity, Atmospheric Refraction, and Gravity, *L. A. Bauer*.

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THE

PHYSICAL REVIEW.

A NEW METHOD OF DETERMINING THE OPTICAL CONSTANTS OF METALS, AND THE OPTICAL CONSTANTS OF SILICON.[1]

By L. R. Ingersoll and J. T. Littleton, Jr.

Introduction.—Considerable attention has been paid in recent years to the optical properties of metals. As is well known, two constants are required to characterize a metal optically, n the refractive index and k the absorption index. When circularly polarized light falls on a well-polished surface of a metal at a certain angle of incidence ϕ (principal incidence), it is reduced to plane polarized light of aximuth ψ (principal azimuth) and the constants n and k are connected with these angles by the relations

$$k = \tan 2\psi; \quad n = \frac{\sin \phi \tan \phi}{\sqrt{1 + k^2}}.$$

Usual Methods.—Aside from the classic experiments of Kundt in measuring the refractive indices of metals in the form of prismatic films, practically all methods of determining optical constants have utilized the property above referred to, whereby a metal surface changes the state of polarization of the incident light. Their points of difference, then, have been chiefly in the various ways in which they have investigated and determined the character of the light reflected from a metal surface on which light of a certain state of polarization had been incident.

[1]Acknowledgment is due for assistance from the Rumford Fund of the American Academy of Arts and Sciences in furtherance of this and correlated work.

The most common type of instrument is the polarimeter fitted with a Babinet compensator. In its usual form this has two quartz wedges, each cut parallel to the optic axis, but with the axis in one parallel to the edge of the wedge, and in the other perpendicular to it. This gives a field of view crossed by dark fringes, and the principal angle of incidence—that which gives a relative change of phase of 90° between the two rectangular components—is determined by noting when the fringe system has been shifted by a quarter of a fringe; the principal azimuth is that which gives the darkest fringes when set for principal incidence. A much better form of Babinet is the Soleil modification used by Drude and others in optical constant determinations. Here a uniformly illuminated field is secured by the use of two wedges each cut parallel to the axis and with their axes parallel, and a plane parallel plate of quartz also cut parallel to the axis, but with its axis perpendicular to those of the wedges. Much more accurate settings are possible with this latter type of compensator.

Of the several other methods may be mentioned the photographic one of Voigt[1] applied by Minor[2] to the measurement of the ultra-violet and visible dispersion of several metals, and the double surface arrangement (Brewster-Jamin) used by Walter[3] which requires no other polarization apparatus than two nicols. Mention may also be made of the recently described method of Bernoulli[4] which determines the principal incidence as that giving the minimum corresponding azimuth. While this yields good results in some cases it has been criticized by Voigt[5] in that it depends on what is only an approximate formula.

Present Method.—The simple method and instrument we are about to describe is an extension to the visible spectrum of an arrangement developed by Ingersoll in connection with some work, not yet published, on the optical constants of metals in the infra-red spectrum. Its advantages are the ease with which determinations may be made, and the fact that for certain classes of metals it

[1]W. Voigt, Phys. Zeitschr., 2, p. 303, 1901.
[2]R. S. Minor, Ann. d. Phys., 10, p. 581, 1903.
[3]B. Walter, Die Oberflächen oder Schillerfarben, Braunschweig, 1895.
[4]A. K. Bernoulli, Ann. d. Phys., 29, p. 585, 1909.
[5]W. Voigt, Ann. d. Phys., 29, p. 956, 1909.

exceeds in accuracy, or at least in the consistency of its indications, the customary (*e. g.*, Babinet) methods. Moreover, the simple optical parts required are such as may be found in almost any laboratory. In effect it is an application of the half-shade or bifield principle so successfully used in polariscopic work, to the problem of analyzing an elliptical vibration. Specifically it concerns itself not so much with the measurement of an elliptical vibration as with the accurate determination of the incidence and azimuth for which this elliptical vibration becomes circular. For if plane polarized light of azimuth ψ is incident on a metal surface at angle ϕ, a circular polarized beam will result on reflection if these angles are those of principal azimuth and principal incidence respectively, and the problem of measuring optical constants becomes that of so determining these angles that a truly circular vibration results from a plane polarized incident beam.

It is in the determination of this circular vibration that the present method differs from others. Instead of getting at the problem from the standpoint of the phase change necessary to produce (or reduce) a given type of polarization, *e. g.*, elliptical, it contrives to take two components of the elliptical vibration at right angles to each other, and by a suitable optical system to have the two halves of the field of view illuminated by these two sections respectively. When, therefore, the two halves of the field show equal illumination and when this condition persists no matter how the observing arrangement is rotated about the axis of the beam, then the polarization of the beam is truly circular. This and other points of the method will be considered more at length in describing the instrument.

Instrument.—The polarimeter is very similar to that customarily used with the Babinet compensator for the analysis of elliptical vibrations, save that this compensator is replaced by our analyzing system. In the present case a Société Genévoise spectrometer was used, the collimator and telescope each being fitted with a nicol in a suitable bearing and carrying a graduated circle. That on the collimator is placed as usual just before the objective. The one on the telescope is of the Glan-Thompson normal incidence type and takes the place of the eyepiece. The slit on the collimator has been,

by means of a suitable diaphragm, supplanted by a circular opening some 4 mm. in diameter.

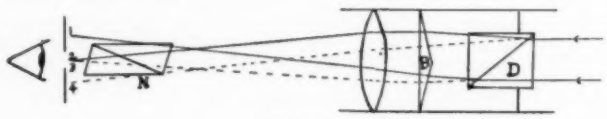


Fig. 1.

Just before the telescope and fastened to it by a suitable fitting is the analyzing system shown in Fig. 1, which, for want of a better name, we may refer to as the "bifield analyzer." *D* is a small Wollaston double image prism of quartz which gives exactly the same separation[1] of the two beams as the biprism *B* behind it. The effect of this optical system, which is similar to that made use of in the Martens-Koenig spectrophotometer, is to give four images (1, 2, 3, 4) of the 4-mm. hole at the slit end of the collimator, these images being focused at the eyepiece end of the telescope. But because the Wollaston prism and biprism each give the same separation, the two middle images (2 and 3) exactly overlap, while 1 and 4 are turned out of the field of view. These two middle images then are the only ones used; they overlap at the focus of the telescope objective, at which focus is an eyepiece diaphragm with a 5-mm. hole. If the eye is placed at this point—there being no eyepiece lens—the field of view will be seen divided into two distinct halves, and each half will be illuminated by one of the two beams from the Wollaston, *i. e.*, the planes of polarization of the two halves of the field are mutually perpendicular. When the analyzing nicol *N* is interposed at the eyepiece end and the field viewed through it, the two halves may be matched with considerable accuracy by rotating this nicol.

Determination of Circular Polarization.—To show the process of analyzing an elliptical vibration, or rather of determining when it is circular, let us imagine telescope and collimator parallel and that the polarizing nicol borne by the collimator is set with its principal section at 45° to each of the two planes of transmission of the Wollaston. The components in each of these planes are then equal and

[1]This equality of separation has been secured in the present case by using a Zeiss variable angle biprism, the cell being filled with a mixture of amyl acetate with a little benzol. An optical worker, however, could readily match a Wollaston prism and a biprism to give separations nearly enough equal.

the analyzing nicol must then be turned so that the two halves of the field show equal illumination. This preliminary adjustment gives the zero setting of the analyzer, which is very nearly at 45° to the planes of the Wollaston, the small difference being due to slightly unequal absorption of the two beams by the optical system. When light of any type of polarization, then, falls on the Wollaston prism, the two mutually rectangular and plane polarized components into which it is separated by this prism are equal when the field of view shows uniform illumination, the analyzer being set at zero. This does not necessarily mean, however, that the polarization of the incident vibration is circular, for, as a glance at Fig. 2*a* shows, any ellipse with its axes at azimuth 45° will give equal components *aa* and *bb*. But now suppose the telescope carrying the bifield analyzer be mounted so that it can be rotated 45° in either direction about its own horizontal axis (not the axis of the instrument). If it is so rotated to one of these positions the components will now be proportional to $a'a'$ and $b'b'$ (Fig. 2*b*) and a difference in brilliancy

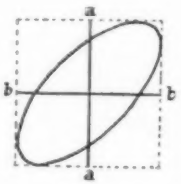


Fig. 2*a*.

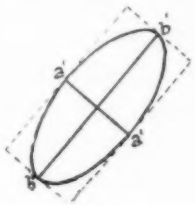


Fig. 2*b*.

of the two halves of the field will result if the analyzer be set at zero; or, what amounts to the same thing, if the two halves are balanced by turning the analyzer, its reading will be other than zero. Any elliptical vibration is thus distinguished from a circular, as the latter would of course give equal components in any azimuth.

Optical Constant Determinations may be made as follows: The instrument having been put in adjustment just as would be an ordinary spectrometer, *i. e.*, the collimator focused to give parallel light, etc., the zero of the analyzer is carefully determined as outlined above. The metal surface to be tested is placed on the table (over the main axis) mounted as usual in a holder with levelling screws, and then has to be adjusted. Some angle of incidence

supposed to be near the principal incidence is then chosen and with the analyzer at zero the azimuth of the polarizer is adjusted to give equality of illumination in the two halves of the field. This will in general yield an elliptically—not circularly—polarized beam which is detected by rotating the telescope right handedly (say) through 45°, when one side of the field will appear brighter than the other. On turning the telescope left handedly then, the other side of the field will be brighter, and not until the azimuth and incidence are such as to give a strictly circular polarization will the field appear uniform no matter how the telescope is rotated. After two or three trials, the setting for principal incidence may usually be made with considerable accuracy, when the angles of principal azimuth and incidence may be taken at once from the circles, and the optical constants computed accordingly.

But while this is the simplest manner of using the instrument, for very accurate work a more systematic series of readings is desirable. The principal incidence having been located approximately as just outlined, two or three points five or ten minutes of arc apart are chosen on each side of it, and for each of these several angles of incidence the following series of readings are taken: (*a*) With the telescope turned to its mean position of rotation—this, as well as the "right 45°" and "left 45°" points, is located by an index mark on the collar of the telescope holder—and with the analyzer at zero, five settings (say) of the polarizer are made for equality of fields. The polarizer is then turned to another angle (less than 90° distant) for which the field is again uniform and a similar series of settings taken. These two angles are denoted respectively as position *A* and position *B* of the polarizer, and the azimuth of the incident polarized light is evidently one half the difference of the two readings. (*b*) With the polarizer at position *A* the telescope is turned to "right 45°" and a series of analyzer settings made for equality of fields. It is then turned to "left 45°" and a similar series made. (*c*) As a check, process (*b*) is repeated, this time for position *B*.

In computing, the series of analyzer readings made for position *A* are plotted, with angles of incidence and mean analyzer settings as coördinates. From such a series, as shown in Fig. 4, the principal incidence is readily determined as that point which gives the same

analyzer readings for both right and left positions of the telescope: these readings should agree closely with the zero setting of the analyzer. A separate determination would be furnished by plotting the series of readings for position B. Having determined the principal incidence, the value of the principal azimuth is readily interpolated for this incidence from the azimuths for the two neighboring angles of incidence; or, better, may be measured for this incidence directly.

Analysis of any Elliptically Polarized Vibration.—It may be well to note that this bifield analyzer can serve in place of a Babinet or other compensator not only for optical constant determinations but also for the analysis of any elliptical vibration. For, as indicated in Fig. 2*b*, if the telescope is turned so that the principal planes of the Wollaston are parallel to the axes of the ellipse, the intensities of the two halves of the field—the analyzing nicol being set at zero—will be proportional to the squares of these axes.

To determine the axes it will be necessary to refer our analyzer readings not to the zero position but to that for which one side of the field is quite dark, *i. e.*, when the principal section of the analyzing nicol is parallel to one of the Wollaston planes. Call the analyzer angle as measured from this point α, and let AB and AC (Fig. 3) be the two components it is desired to measure. Then if the analyzer is set for equality of fields its plane will make angle α with AC (say) and the component in either field will be AD. Then the ratio of AC to AB is evidently tan α. This is on the assumption of no unequal absorption of the two beams. Since in general there is some such absorption, however, it is allowed for by taking account of the zero analyzer setting. Calling this angle β —measured from the same point as α—the ratio of the two components is given by tan α/tan β. When the telescope is turned so that this ratio is a maximum it gives the relative values of the elliptical axes.

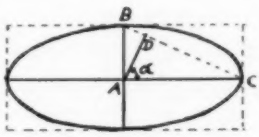


Fig. 3.

Sources of Error.—Before discussing the accuracy of determination possible with this form of instrument some few criticisms may be passed upon it. It would undoubtedly be better to locate the

analyzing nicol directly behind the bifield analyzer and thus avoid any possible "depolarizing" action of the objective. However such an effect, while it doubtless exists in small degree, has not been noted and may probably be safely neglected. Another point that may be mentioned is that, because of the lack of an eyepiece, the eye of the observer focuses practically on the metal surface and any scratches or defects show up very prominently. This objection is offset, however, by the fact that the optical constants can, for this reason, be determined for a very small spot, that is, where the surface is best. The fact that the dividing line of the field is turned now to the right and now to the left may at first sight appear a hindrance to accurate reading, but a little experience shows that this is no real objection.

Accuracy of Observations.—No pretense has been made of an exhaustive study of the instrument with a view of determining its possible accuracy of measurement under given conditions; but as one of us (Littleton) has had considerable experience with both forms of the Babinet compensator as used in optical constant determinations, the comparison which this fact makes possible may be of interest.

In the first place it is to be pointed out that the accuracy of measurement to be expected from this or any other method depends on two somewhat separate conditions. These are, first, the absence of any overlooked source of error or mistake in principle; and second, the consistency with which it will repeat its indications. As regards the first point it may be said that the present method shares with the Babinet and other commonly used schemes, any uncertainty which arises from the application of the laws of metallic reflection; but that it contains any hidden source of error of any importance not common to these methods, we believe the simplicity of its principle forbids. This is all on the assumption that the metallic surfaces to be studied are perfect both as to planeness and polish: whether variations from this ideal condition will produce a greater or less disturbing effect with the present instrument, than with the Babinet, remains for further investigation. With respect to the consistency of successive observations it is easier to speak with positiveness, and this will be considered in discussing the constants of silicon.

Measurements have been made on three widely differing metals, optically speaking, viz., silver, steel and silicon. As it is not believed that the optical constants of the latter metal have been discussed before,[1] they will be considered at some length. With regard to the measurements on silver and steel it is sufficient to state that they indicate, both from their self consistency and their agreement with accepted values, that the accuracy of the method as applied to metals such as these is somewhat greater than that of the first form of Babinet, although hardly exceeding, if indeed it equals, that of the latter form. It may well be stated, however, that the accuracy of the Babinet, particularly in the determination of principal azimuth, is not uniform for all metals but is less when the azimuth is small.[2] On the other hand, with our method the reverse is true, and it may be considered then, not so much competitive as complementary to the Babinet method. For while our instrument may not exceed or even equal in accuracy the best form of Babinet for the majority of metals, it is believed that it will prove superior for those metals which give small principal azimuths, as may be indicated by the following results.

Optical Constants of Silicon.[3]

The silicon surface used was one of the best polished and tested with the Babinet form of polarimeter by Littleton sometime since. It was from a piece of 99.75 per cent. purity furnished by the Carborundum Company of Niagara Falls. The grinding and polishing had been done with graded carborundum, finishing with dry rouge

[1]Since the above was written, measurements on silicon have appeared in a paper by H. v. Wartenberg (Deutsch. Phys. Gessell. Verh., 12, p. 105, 1910). His results, viz., $n=3.87$; $k=0.116$, are in fair agreement with the present, and the outstanding discrepancy may possibly by explained by the fact that his specimen was only 95 per cent. pure.

[2]That is, the actual error of setting is practically the same for small as for large azimuths, hence the percentage error is much greater for the former.

[3]We shall not discuss here the question of whether silicon is entitled to be considered as a metal, optically speaking. However it may be added that Littleton has found that its reflecting power at $\lambda=9\mu$ is practically the same as in the visible spectrum, while Ingersoll has recently measured the optical constants as far as $\lambda=2.25$ in the infra-red and found them almost independent of wave-length, showing, if anything, a slight decrease of refractive index with increasing wave-length. Both of these effects would be more characterictic of a dielectric than a metal.

on chamois. The disturbing effect of the few scratches had been previously tested and found negligible.

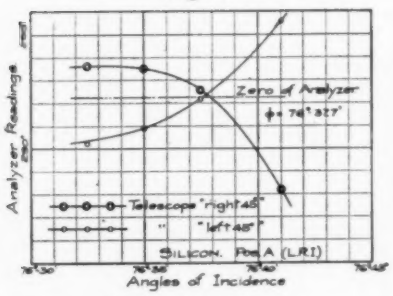
The measurements are tabulated briefly in Table I.

TABLE I.

Observer.	Position of Polarizer.	Principal Incidence.	Principal Azimuth.	n	k
J.T.L.	A	76° 34.5′	2° 44′	4.05	0.096
J.T.L.	B	76° 34.1′			
L.R.I.	A	76° 37.7′	2° 40′	4.08	0.093
L.R.I.	B	76° 37.1′			

The graphical computation for one of the four sets is illustrated in Fig. 4. While the points do not lie especially well on any simple curve, the principal incidence can still be taken to the nearest minute of arc at any rate. It is to be noted that the point where the two lines cross, that is, where the analyzer readings for the "right 45°" and "left 45°" positions of the telescope are the same, agrees very well as it should, with the zero setting of the analyzer. It does not always agree as closely as this.

Fig. 4.



Angles of Incidence.

The mean of all the measurements gives for the constants of silicon, $n = 4.07$, and $k = 0.095$, computed from the angles 76° 36′ for principal incidence, and 2° 42′ for principal azimuth. Its reflecting power calculated from these constants is 37.1 per cent. The mean of all the Babinet determinations on several different plates is $n = 4.14$ and $k = 0.15$.

As to the self consistency and accuracy of the determinations it is to be noted that with the present method the results for principal incidence, as determined by two different observers, varied hardly

1′ from the mean, and the azimuth only 2′. Successive settings for azimuth could be made indeed with a variation hardly larger than the smallest reading of the polarizer circle, *i. e.*, 5′. With the Babinet the principal incidence can perhaps be determined to the same order of accuracy if the mean of a large enough series of readings is taken. Successive settings for principal azimuth, however, show a much greater variation, amounting to some two degrees with the older form of Babinet and nearly a degree with the Soleil modification.

It may be noted that the determinations of the principal azimuth with the Babinet come somewhat higher (about 1°) than with the present method, as the above comparison shows. No reason can be assigned for this, although it is probably an effect depending on the particular character of the surface rather than one that indicates any real discrepancy between the two methods. For, as already pointed out, given surfaces of perfect planeness and polish, either method of analysis of the reflected ellipse—that is, by the phase relations of the two components (Babinet), or simply by the ratio of its axes (present method)—should give the same result; but the disturbing effect of departures from this ideal condition remains to be determined.

PHYSICAL LABORATORY,
UNIVERSITY OF WISCONSIN,
May, 1910.

STUDIES IN LUMINESCENCE.

BY EDW. L. NICHOLS AND ERNEST MERRITT.

XIV. FURTHER EXPERIMENTS ON FLUORESCENCE ABSORPTION.

IN the fourth paper of this series we have used the term fluorescence absorption in referring to the increase of the absorbing power of a fluorescent substance which results from fluorescence. Such an effect was first observed by Burke,[1] who found a considerable increase in the absorption of uranium glass when the glass was excited to fluorescence. The writers observed the same effect in solutions of fluorescein and eosin.[2] The increase in the absorption appeared to be greater for those wave-lengths which corresponded to the brightest regions of the fluorescence spectrum. Camichael,[3] upon repeating these experiments, was unable to detect any change of absorbing power during fluorescence either in the uranium glass used by Burke or in the fluorescent solutions tested by us. The question was again attacked in 1904 by Miss Wick,[4] who made a detailed study of the phenomenon in the case of an alcoholic solution of resorufin. Her results consistently showed an increase in the absorbing power of the solution during fluorescence, and were in complete agreement with the results obtained by us with fluorescein and eosin. More recently a method of detecting the effect, if it exists, has been suggested by Wood,[5] and a few trials of the method by him led to negative results. The most recent experimenter in this field is Houstoun,[6] whose very careful experiments also fail to give any indication of a change in absorption due to fluorescence.

The results obtained by ourselves, and especially those obtained by Miss Wick, were so definite and positive that until recently we have been of the opinion that the failure of others to observe the effect was due to the fact that they had not chosen suitable

[1] Burke, Philosophical Transactions, Vol. 191 A, p. 87, 1898.
[2] Nichols and Merritt, PHYSICAL REVIEW, Vol. 19, p. 397, 1904.
[3] Camichael, Comptes Rendus, Vol. 140, p. 139.
[4] Frances G. Wick, PHYSICAL REVIEW, Vol. 24, p. 407, 1907.
[5] R. W. Wood, Phil. Mag., Vol. 16, p. 940, 1908.
[6] R. A. Houstoun, Proc. Royal Society of Edinburgh, Vol. 29, p. 401, 1909.

conditions for the experiment. We were led to suspect the existence of some systematic error, however, by the results of a careful study of the collimator slit of the spectrophotometer used in our recent experiments upon the distribution of energy in fluorescence spectra. It was found that the screw was a very accurate one and that the opening of the slit was very closely proportional to the reading of the micrometer screw. To test this point the slit was mounted in a lantern and the enlarged image was measured for a large number of different readings of the micrometer. The results are shown in Fig. 94.

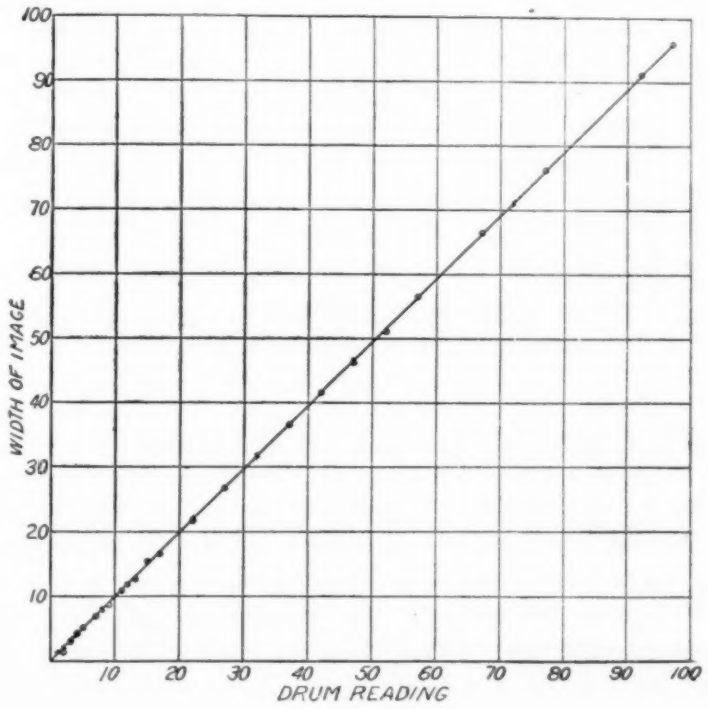


Fig. 94.

We then tested the amount of light passing through the slit at different widths by balancing two acetylene flames against each other, the adjustment being made by varying the slit width in one case and by varying the distance of the flame in the other. The experiments were performed in a dark room with an elaborate sys-

tem of screens to prevent reflections, and several independent tests convinced us that the inverse square law of distances was very exactly satisfied. If the intensity is computed by the law of inverse squares, and if a curve is plotted showing the relation between intensity and slit width, the results obtained are of the type illustrated in Fig. 95.

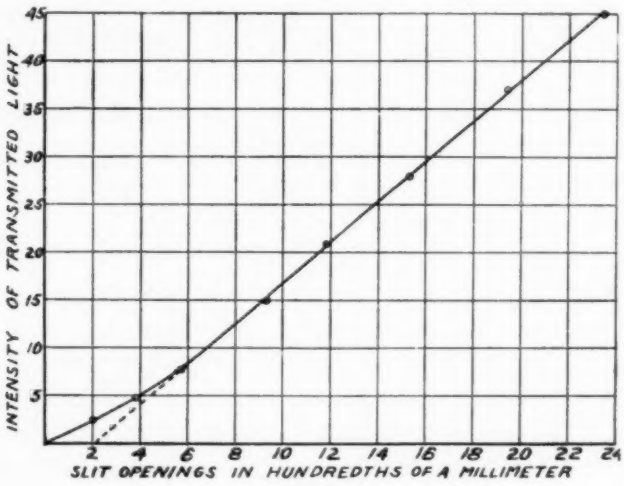


Fig. 95.

It will be seen that for narrow slits the intensity of the transmitted light is not proportional to the slit width. When the width exceeds a few hundredths of a millimeter the line becomes practically straight, so that equal increments in slit width correspond to equal increments in intensity. The conditions, whatever they are, which lead to the curve in the neighborhood of the zero of Fig. 95 are equivalent in their effect to a shift in the zero point of the screw by about two divisions. The intensity transmitted by a slit 50 divisions wide is not twice as great as that transmitted by one 25 divisions wide, but the ratio is in reality 48 to 23.

These experiments were not made with the same instrument that had been used by ourselves and later by Miss Wick, but refer to an exactly similar Lummer-Brodhun spectrophotometer. It seems probable that this effect, due possibly to diffraction or to reflection from the jaws of the slit, is common to all instruments of this type.

It is clear that if the effect is disregarded, indications of fluorescence absorption may be obtained even if no such effect exists. The method used by Miss Wick and by ourselves involved three readings; namely, the intensity of the fluorescent light alone, the intensity of the light transmitted by the non-fluorescent solution, and the combined intensity when light was transmitted through the solution at the same time that the latter was excited to fluorescence. The sum of the first two readings being found greater than the third, it was assumed that the transmission in the latter case was less than in the first. If, however, each of these readings of intensity had been too great by two divisions, as indicated by Fig. 95, the result of such procedure would be to give an apparent fluorescent absorption measured by two divisions.

While it is difficult to see how this source of error alone could account for results of the character obtained by Miss Wick and ourselves, the detection of one source of systematic error made it appear possible that other similar errors might be present, and has led us to take up the study of this question anew. The result of the numerous experiments which will be briefly described in this paper has been to convince us that the phenomenon of fluorescence absorption either does not exist, or that the effect is so small that the methods thus far used for its detection are inadequate.

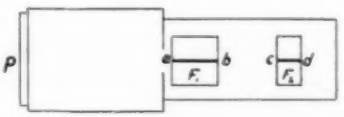


Fig. 96.

In the first method used an attempt was made to obtain a photographic record of the effect. The arrangement is shown in diagram in Fig. 96.

The large square cell F_1, containing a solution of fluorescein, was excited from above by a narrow beam of light, so that a central layer *ab* was excited while the rest of the solution was not. Directly back of this was another cell F_2, also illuminated from above so that the narrow vertical strip *cd* was excited. The photographic plate *P*, suitably screened from all sources of light except the fluorescence in F_1 and F_2, would be fogged nearly uniformly over its surface by the light from *ab* if this alone was excited, and the fogging would also be practically uniform if *cd* was excited. If, how-

ever, that part of the liquid in F_1 which is excited to fluorescence acquires the power of absorbing the fluorescent light more strongly than before, then we should expect *ab* to cast a shadow upon the photographic plate. While this shadow could not be expected to be very sharp or very dense, the results obtained by ourselves and Miss Wick indicated that under suitable conditions it ought to be clearly visible in the negative.

Extended efforts were made to obtain such conditions of concentration, thickness of layer, intensity of excitation, etc., as would bring out the expected shadow on the plate P. Over 100 negatives were made and many of these were under conditions which

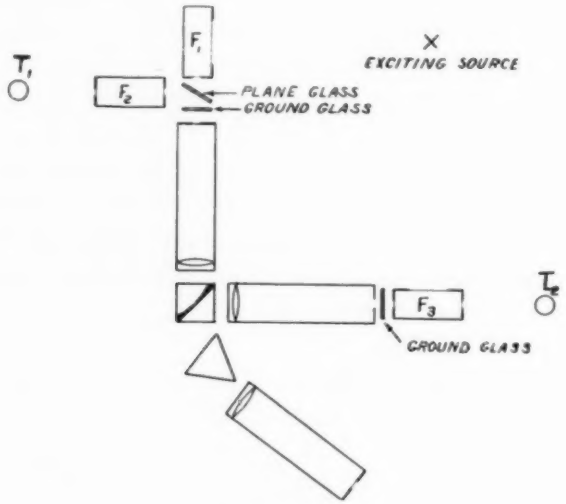


Fig. 97.

appeared to us to correspond to those under which the spectrophotometer had indicated a large fluorescence absorption; but in no case was a definite shadow observable.

The next method of testing the matter is shown in diagram in Fig. 97. Three cells containing a solution of fluorescein, or in some cases resorufin, were used as shown in Fig. 97. F_1 and F_3 were excited by the same source so as to eliminate errors due to variations in excitation; the source used was sometimes a quartz mercury lamp and in other cases the tungsten lamp. Since the solution was

exactly the same in all three cells, and since F_1 and F_3 were at nearly the same distance from the exciting source, the two collimator slits were illuminated with almost equal brightness. Any slight inequality was balanced by opening or closing one of the slits. This adjustment being made, the exciting source was extinguished and light was sent through the cell F_3 from a small tungsten lamp, T_2. To balance this illumination, light from another tungsten lamp, after passing through the cell F_2, was reflected by a piece of plane glass into the second collimator slit. The balance was obtained by adjusting the distance of T_2, which slid upon a graduated photometer track. When this balance was obtained the exciting source was again started and the field of the spectrophotometer observed. If the effect of fluorescence is to increase the absorbing power of F_3 we should expect that while fluorescence alone and transmission alone give a perfect balance, there would be a lack of balance when excitation and transmission occur simultaneously. When satisfactory conditions of steadiness were obtained no such disturbance of balance could be observed. A sample set of readings is given in Table I. The small positive result obtained in this case is smaller than the errors of observation. In other cases the results indicated a small decrease in absorbing

TABLE I.

Resorufin. Excited by Mercury Arc.

Slit in front of F_3 set for equality of fluorescence alone. Readings 51.6, 49.7, 50.7, 50.7. Slit set at the average 50.7.

Lamp T_2 set for $F+T$, *i. e.*, fluorescence and transmission together. Distances =233, 245. Average 239.

Lamp T_2 set for transmission alone (T) 233, 233. Average 233.

$F+T$, 226, 228. Average 227.

Slit set again for equality of fluorescence alone. Readings 40.7, 50.4, 50.3, 50.7. Slit set at the average 50.3.

$F+T$: 235, 239. Average 237.

T: 243, 245. Average 244.

$F+T$: 226, 237. Average 232.

Slit set for F alone: 50.8, 50.8, 50.7, 50.6. Average 50.8.

$F+T$: 238, 243. Average 240.5.

T: 240, 236. Average 238.

$F+T$: 243, 237. Average 240.

Average of all: Distance of lamp for T alone =238.3; for $T+F$ =236.0.

If this difference is real it indicates that the absorption of the solution during fluorescence exceeds its absorption when unexcited by 1.7 per cent.

power during fluorescence. The experiment was tried with solutions of different concentration and different intensities of excitation. But when satisfactory conditions as regards steadiness were obtained no disturbance of balance could be detected which was greater than the errors of observation.

It was suspected that the phenomenon of fluorescence absorption apparently demonstrated by Miss Wick and ourselves might indicate not an increase in the absorbing power of the solution but rather a decrease in its power of fluorescing. The results obtained by us might be interpreted equally well in either of these two ways. The fact that fluorescence absorption seemed to be in proportion to intensity of fluorescence in different parts of the spectrum lent strength to this view. If the effect is a diminution of fluorescence and not an increase in absorption the failure of our photographic tests could also be explained in an obvious manner.

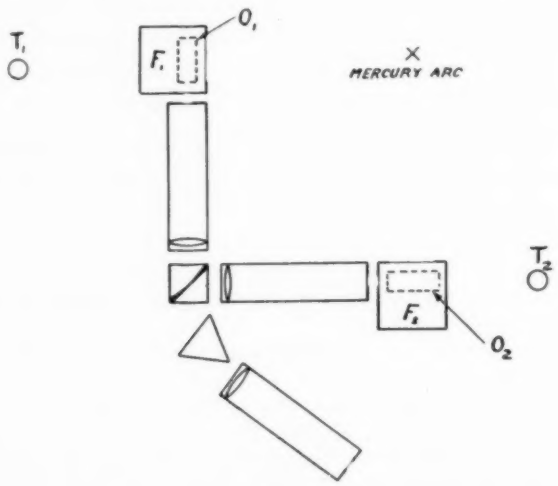


Fig. 98.

If the fluorescence is diminished we should expect the diminution to be observable not only along the line of the transmitted light but in other directions. To test this matter we set up two large fluorescent cells F_1 and F_2 (Fig. 98) covered with black paper except on the sides towards the exciting mercury arc, and having two openings O_1 and O_2 in the bottom through which the light of the

tungsten lamps T_1 and T_2, after reflection from mirrors, might pass up into the cell. The balance having been obtained with fluorescence alone, the lamp T_1 was then turned on and we tried to determine whether there was any change in the balance resulting from extinguishing T_1 and at the same time lighting T_2. The only effect was a slight one, opposite in sign to that which would be indicated in fluorescence absorption, and due undoubtedly to a small amount of stray light entering the slit after reflection from the walls of the cell.

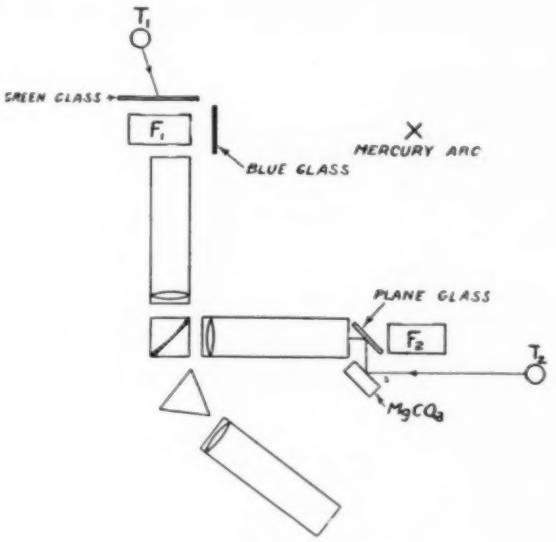


Fig. 99.

It seemed to us possible that the effect might be analogous to the effect of infra-red rays in suppressing fluorescence, and that possibly it might be produced not by the visible rays which caused this annoyance through stray reflection, but by the red or infra-red rays. We therefore interposed ruby glass in the path of T_1 and T_2, thus eliminating disturbances due to stray light. Under these circumstances no disturbance of balance resulted from extinguishing one lamp and lighting the other.

It seemed possible that while fluorescence absorption might really be the result of a diminution in the intensity of fluorescence this decrease might not be the same in all directions but might be great-

est in the direction in which transmitted light proceeded. The arrangement of apparatus shown in Fig. 99 was intended to test for the effect in directions nearly but not quite the same as the direction of transmitted light. The light from the tungsten lamp T_1 passes through the cell F_1 so as not to fall in the slit of the instrument both being nearly parallel to the axis of the collimator. The small amount of stray light from T_1 which unavoidably did reach the slit was balanced by light from the second tungsten lamp T_2 as shown in the figure. The results were entirely negative. Thinking that the intense green line of the mercury arc might pro-

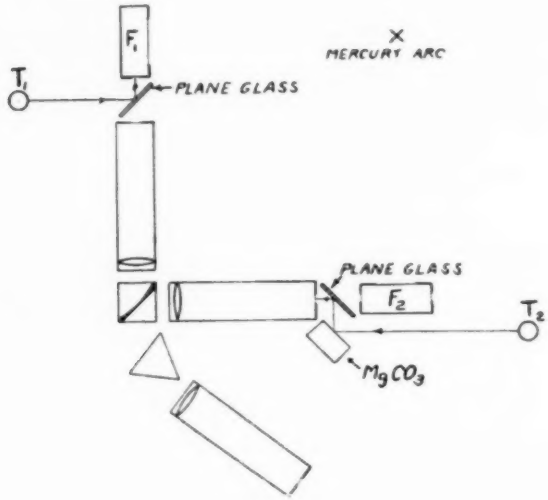


Fig. 100.

duce so much effect in weakening the fluorescence in F_1 that additional light from T_1 would produce only a slight effect, we interposed in some cases blue glass as shown, and in order to diminish the excitation produced by the light from T_1 we sometimes used green glass as indicated. The results, however, were in all cases negative.

In Fig. 100 is shown an arrangement for testing the effect of transmitted light upon fluorescence in case the direction of transmission is opposite to the direction in which fluorescence is observed. No effect could be detected.

In Fig. 101 are shown the essential parts of the apparatus used in applying the method suggested by Wood. A disk, shown in detail at the right of the figure, was arranged so that the four sectors might either occupy the position shown in the upper diagram, or might be shifted with reference to each other so that the inner openings and the outer openings would be alternate. This disk was mounted between the exciting source and the fluorescent cell *F*, as shown. Light passed through the outer sectors to excite fluorescence, and light passing through the inner sector, after reflection from a block of magnesium carbonate, passed through the cell

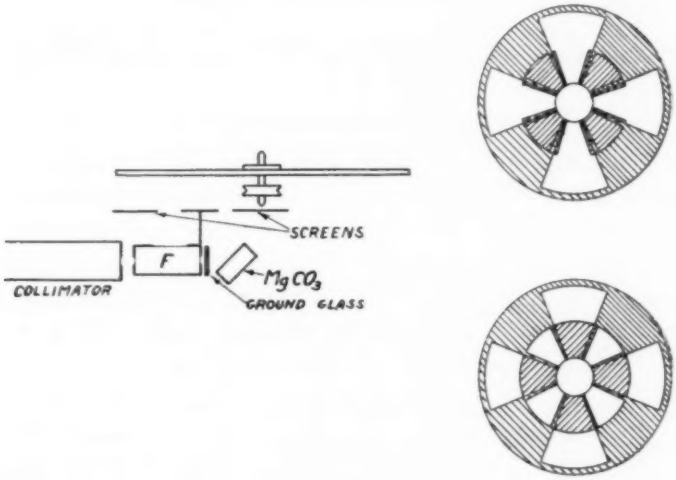


Fig. 101.

to the collimator slit. Having balanced the illumination against a standard placed before the second collimator for the case where the inner and outer sectors were open alternately, the disk was then changed so as to make the excitation and transmission simultaneous. The results of several sets of observations with this apparatus are given in Tables II.–V. The observations indicate a slight *negative* effect, that is, the transmission of the solution appears to be greater during fluorescence. But the effect indicated is so small that we are inclined to look upon it as resulting from accidental errors.

A few measurements were made by a method essentially the

TABLE II.

Fluorescein. Moderate Concentration. Woods' Method.

The numbers in the table give the width of the slit near *F* (Fig. 101) when set to a balance with the standard in front of the other slit.

$\lambda = 0.523\,\mu$.

Sectors Open Alternately.		Sectors Open at Same Time.	
100.9		101.2	
97.7		100.2	
104.2	Average 101.58	100.5	
103.5		101.2	Average 100.78
100.5		102.0	
101.7		98.8	
100.0		100.7	
100.4	Average 100.65	98.7	Average 100.05
Final average = 101.11		Final average = 100.41	

TABLE III.

Resorufin. Dilute. Woods' Method. $T = 0.18F$. $\lambda = 0.599\,\mu$.

Sectors Open Alternately.		Sectors Open at Same Time.	
113.4		111.2	
112.2		112.4	
114.7		112.3	
	Average 113.4	111.9	Average 111.95
112.4		112.3	
113.8		113.7	
113.3		113.4	
114.7	Average 113.7	112.8	Average 113.05
Final average = 113.55		Final average = 113.0	

Fluorescence absorption = $-.033T$.

TABLE IV.

Resorufin. Dilute. Woods' Method. $T = 1.02F$. $\lambda = 0.599\,\mu$.

Sectors Open Alternately.		Sectors Open at Same Time.	
64.6		66.2	
65.2		64.4	
67.3		65.4	
66.8	Average 65.98	65.7	Average 65.42
66.6		66.8	
66.4		65.9	
66.5		66.2	
66.9	Average 66.68	66.3	Average 66.30
Final average = 66.33		Final average = 65.86	

Flourescence absorption = $-.014T$.

TABLE V.

Resorufin. Dilute. Woods' Method. $T = 7.27F$. $\lambda = 0.599\,\mu$.

Sectors Open Alternately.		Sectors Open at Same Time.	
20.6		19.0	
20.1		19.4	
20.6		19.8	
20.1	Average 20.35	20.0	Average 19.78
20.3		20.0	
19.9		20.3	
20.4		20.5	
20.4	Average 20.25	20.7	Average 20.38
Final average = 20.30		Final average = 20.08	

Fluorescence absorption = $-.012T$.

same as that used by us in 1904, except that the source of the light transmitted was the fluorescence of a portion of the solution. A dilute solution of fluorescence was contained in a cell 20 cm. long, so arranged that either the half nearest the slit or that at a distance could be screened from the exciting light, which in this case was the mercury arc. The spectrophotometer was set for a wave-length near the crest of the fluorescence spectrum and not overlapping either of the mercury lines, so that errors due to stray light were excluded. Upon screening that part of the cell lying nearest the slit the field was illuminated by the fluorescence light of the distant part of the cell after transmission through the rest of the cell T. Upon screening the distant part of the cell the light received in the instrument was due to the fluorescence of the nearer part F. Upon removing both screens fluorescence and transmission occurred at the same time C. If absorption is increased by fluorescence we should have

$$F + T > C.$$

The readings in one case are given in Table VI.

The observations contained in Table VI. indicate a positive fluorescence absorption of 15 per cent. But if we apply the additional zero correction called for by the calibration curve of Fig. 2 the difference between $F+T$ and C is reduced to 0.9 div. or 4.3 per cent. In other cases an equally large negative result was obtained.

The results of all of these experiments, which have been repeated

TABLE VI.

	T	C
23.7	23.2	
23.7	23.4	
22.9	23.6	41.2
23.4	22.9	41.2
Average 23.42	Average 23.28	Average 41.2
Zero 2.4	2.4	2.4
$F=21.02$	$T=20.88$	38.8

$$F+T-C=41.9-38.8=3.1=0.15T.$$

many times, and performed with more precautions to avoid false results than can be indicated in this brief account, has been to convince us that the previous results of both ourselves and of Miss Wick are due to some systematic error, and that the supposed increase in absorption due to fluorescence either does not in reality exist or is too small to be detected by these methods. We have not been able to determine the exact nature of the error which led to our preceding results. The peculiar relation between slit opening and intensity brought out in Fig. 95 will explain some of the results but not all. Another source of error which might have been an important one is that resulting from the neglect of the slit width correction, to the importance of which we have directed attention in an earlier article of this series. Unfortunately the photometer with which the original observations were made is in use in another piece of work under such conditions that we have not been able to examine it with particular reference to these points.

A NOTEWORTHY INTERRELATION OF ILLUMINATING POWER, DENSITY, AND VISCOSITY OF CERTAIN KEROSENE OILS.

By G. W. Stewart.

CHEMISTS have devoted much attention to kerosene oil and the results obtained have been of great assistance in the production of the present excellent quality of burning oil. The complex character of the oils has seemingly discouraged any investigations save those employing chemical methods. This paper, which is a report of certain progress made in an investigation of kerosene oil from the standpoint of the physicist, contains results of scientific interest which are worthy of record; but its chief value rests in the demonstration of the possibility of obtaining valuable results by physical methods of investigation. The study was undertaken in the belief that facts could be ascertained which would be not only of definite scientific value, but also of direct benefit to both refiners and consumers through improvement in the legal requirements.[1] Conditions have necessitated the indefinite postponement of a continuation of these experiments and the results obtained up to the present time, though not satisfactorily comprehensive in application, are published in the hope that the work may be continued elsewhere.

The best bibliography on the subject of kerosene oils is found in Vol. II. of Redwood's "Petroleum and Its Products." Practically all the results here recorded are new; but where similar experiments have been previously attempted references are made at the appropriate point in the body of the paper.

Apparatus.—A detailed description of the apparatus used is unnecessary as both the apparatus and its degree of accuracy are familiar to physicists. A two-meter photometer bar, a Lummer

[1]The experimental work was performed at the University of North Dakota under the auspices of the North Dakota State Oil Inspection. An abstract of a preliminary report to the American Physical Society appears in Phys. Rev., XXVIII., 1909, p. 65.

Brodhun screen, primary and secondary incandescent lamp standards, storage cells, a standard ammeter, a small hand lamp with a number two Queen Anne burner, an ordinary laboratory balance and other minor pieces of apparatus were used in the experiments here recorded.

Method of Measuring "Illuminating Power."—The term "illuminating power" is rather indefinite. In this paper it will mean the candle power-hours-per-gram, the candle power being measured in one direction only, and that perpendicular to the plane of the flat flame.

The lamp was placed in one pan of a balance located at the end of the photometer bar, the flame being adjusted always at the same point on the bar with its plane perpendicular to the latter. Five grams of oil were burned, the time required being obtained with a stop watch. Observations with the photometer screen were made every half minute. The value of candle power and time were plotted and the area utilized to find the candle power-hours-per-gram. The result could be relied upon to within one per cent. A secondary incandescent lamp standard was used as a standard of comparison throughout the entire experiments. The candle power of the source of comparison was thus independent of atmospheric conditions.

On the other hand, the measured candle power-hours-per-gram or "illuminating power" of the kerosene varied with changes in atmospheric conditions. In as much as the results found at different times could not be directly compared, an indirect means was obtained through measurements of a certain sample made during each set of experiments. All results were then reduced to 0.310 candle power-hours-per-gram for the standard sample. This sample was a very good grade of oil and in all probability did not change in composition during the experiments.

Variation of "Illuminating Power" with Height of Flame.—The results of this test were that the illuminating power was a maximum with a flame height of 2.5 cm., whereas at 1.7 cm. and at 3.3 cm. it was five per cent. less. Observations for various heights were obtained and a curve drawn. It thus became possible to correct for any variations in flame height. During these observations drawings were made of the shape of the flame by tracing the image which was

thrown by a lens upon a sheet of squared paper. From these drawings it can be shown that the candle power per unit area increases with decrease in height, changing more than 40 per cent. beween the limits of height already stated.

Whether or not this change can be wholly accounted for by the various thicknesses of the flame was not ascertained. The reason for a maximum illuminating power is probably that we have the combined action of the screening of the flame by the burner and the decrease of efficiency with decreasing thickness of the flame. It would be of practical importance to investigate as to whether or not the thickness of the wicks in present use give the most efficient flame.

Variation of Illuminating Power with Time of Burning.—It has been shown[1] that fractionation of crude petroleum can be obtained by filtration; and it would not be wholly unexpected if a difference in the illuminating power could be detected when the oil is burned for a considerable length of time. A quantity of oil sufficient for several hours burning was taken and measurements made on the illuminating power at different times. No variation greater than the errors of the experiment was found.

A check upon the conclusion was made by the measurement of the possible change in density. The density of a good sample was carefully measured, 80 per cent. of the oil burned off, and the measurement repeated. No variation in density to within one part in ten thousand was detected. Elliott[2] finds that the oil used in a lamp replenished from day to day during one week is practically the same character at the end of the week as at the beginning.

Variation in Illuminating Power with Different Wicks.—Redwood[3] claims to have found six per cent. variation when wicks of different weave were used. Careful observations with the best and the poorest wicks used throughout these experiments showed that the variation in candle power-hours-per-gram was within the experimental error, viz., one per cent. While no effort was made to disprove

[1]The fractionation of crude petroleum by capillary diffusion; Gilpin and Cram, Bulletin 365, U. S. Geological Survey, 1908.

[2]The illuminating value of petroleum oils; a paper presented to the Illuminating Engineering Society, October 5–6, 1908.

[3]Petroleum and its Products, Vol. III., p. 543.

Redwood's conclusions my experience would cause me to doubt their accuracy.

Relative Influence of Surface Tension and Viscosity.—The surface tension of the various oils in the market vary, but only to a small extent.

Measurements on eighteen samples taken at random, with densities (at 60° F.) varying from 0.7852 to 0.8032, showed an extreme variation of surface tension of approximately two per cent. Viscosity is a much greater factor. The object of the wick is not merely to raise the oil to a certain height, but it must feed the oil with sufficient rapidity.

Only factors which materially affect the flow of the oil need be studied. The samples which varied in surface tension two per cent. varied in coefficient of viscosity sixty per cent. The viscosity was measured by a method described at another point in this report. The variation in viscosities is very important.

Illuminating Power and the Usual Tests.—Reference is here made to the flash test, the fire test, the density, the residue and the relative viscosity. Preliminary tests with samples of oil obtained at different times and from different refineries showed no definite relation between the illuminating power and any one of these physical tests. It was found that, in a general way, an increase in relative viscosity or in residue indicated a decrease in illuminating power. Measurements of the flash test, the fire test, and the residue were made by Professor E. J. Babcock and Miss Marcia Bisbee, of the Department of Chemistry of the State University of North Dakota, I wish to take this occasion to express my appreciation of their coöperation.

Illuminating Power of Distillates, Showing the Variation with Density.—The conclusion might be derived from the previous paragraph that there is no connection between the illuminating power and density; and this is correct when comparison is made with different samples of oil. It was found, however, that when distillates of one sample of refined oil were used, there was a variation with density which is definite.

Two such tests were made, the distillates being from two different samples. The results are given in the accompanying Fig. 1.

Curve 1 was obtained with distillates produced in the following temperature ranges: up to 155° C., 155° to 227° C., and 227° to 299° C. Curve 2 records the results obtained with distillates obtained from a large refinery. These refinery distillates were obtained in such a manner that they can hardly be said to be of one sample, but only approximately so.

In computing the illuminating power correction was made for differences in flame height in accord with the results already described. The difference between the two curves is due in part to

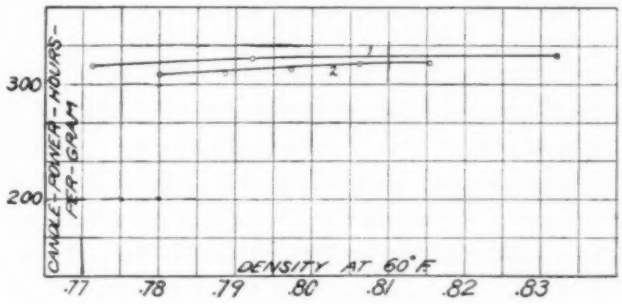


Fig. 1.

the fact that no allowance was made for different atmospheric conditions and in part to the fact that the distillates were not obtained in the same way. It is evident that the more dense components of the oil really have the greater illuminating power.

Similar results have been obtained by Dr. Geo. W. Gray, now of the Paola Refining Company, but they have never been published. The conclusions from the curve must not be extended to a comparison of the illuminating power of different samples of oil. Neither can it be concluded that the above oils would be more satisfactory if some of the lighter components had been distilled off, for the question of viscosity and the flow of the oil in the wick is a practical one that must be considered.

Measurement of the Coefficient of Viscosity and its Change with Temperature.—The results recorded in the above paragraphs suggested a theory which deserved testing. For this theory more accurate measurements had to be made than are possible with the viscosimeter used in oil testing. Moreover the results were desired

in absolute rather than relative units. The measurement of the time of flow of a given quantity through a capillary tube was adopted as the most convenient and at the same time sufficiently accurate. The formula used was

$$n = \frac{\pi p t R^4}{8VL} - \frac{dV}{8\pi Lt}.$$

In this equation, n is the coefficient of viscosity, p is the average pressure employed, t the time of flow, R the radius of the capillary, V the volume of the oil used, L the length of the tube, and d the density of the oil. The second term, which represents the kinetic energy correction, could not be neglected. The cross-section of the tube was an ellipse. The correction for this when applied according to Thorpe and Roger[1] was not large enough to consider. The limit of applicability of the above formula occurs when the mean velocity becomes $1{,}000 \times n/dR$. The tube used was 75.5 cm. long and had an average internal radius of 0.0498 cm. The above critical velocity is 250 cm./sec. The mean velocity in the above experiments did not exceed 66 cm./sec. The accuracy of the method was tested by distilled water, and a constant error of about two per cent. found. The apparatus could have been improved quite easily, but its results are amply accurate for the comparisons made in the coefficients of viscosity.

The variation of the coefficient of viscosity with temperature had to be determined in order to compare the results obtained at different times. Observations were made with changing temperature using a very good sample of oil. The variation of temperature was that occurring in the experiments described in this report, viz., 18° to 25° C. In this range the curve drawn with coefficients and temperatures as coordinates was practically a straight line. The correction at 20° C. was about 1.6 per cent. per degree Centigrade. All measured coefficients were reduced to the values at 20° C. by means of this result. In other words, all the oils were assumed to have the same temperature coefficient. It is thought that the error caused by this assumption is not sufficient to affect the conclusions contained in this paper.

[1]Thorpe and Roger, Phil. Trans. A, 1894, Pt. II., pp. 445–449.

Viscosity and Density of Distillates.—Preliminary measurements of the relation between the viscosity and the density of distillates indicated that there was a definite relation. This was further verified by accurate measurements of the coefficients of viscosity. The accompanying curves in Fig. 2 indicate the relations found in two

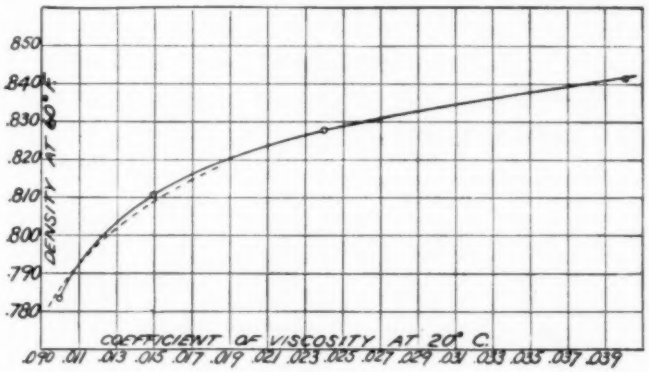


Fig. 2.

series of experiments. The full line shows the relation with four distillates obtained by the distillation of an excellent sample of oil, and the dotted line shows the results obtained with the refinery distillates, to which reference has already been made. For the purpose of this report the former curve will be the one utilized, but the significance of the results would not be changed if the latter curve had been chosen.

The values of the density are those at 60° F., and the values of the coefficients of viscosity are those at 20° C. Apology is made for the use of two different scales of temperature. The values for density of the oils are usually given at 60° F.

Relation between Illuminating Power and Viscosity Ratios.—As indicated by the foregoing, if the distillates of one sample are used in the comparisons there seems to be a definite relation between illuminating power and density and between viscosity and density. On the other hand, if different samples, which of course have different densities, are used, there is no such relation obtained. A careful consideration of these facts led me to believe that there are present undesirable compounds which affect[1] both the illuminating

[1]It might be thought possible for the variation in viscosity to affect the illuminating

power and the viscosity, but without a correspondingly great variation in the density. If this conclusion is correct, then we should expect to find that the illuminating power and the viscosity vary in the same sense. The following method of testing the theory was adopted. Consider Fig. 2 (full line) as expressing the "ideal" viscosities of kerosene oil at different densities.

TABLE I.

Sample Number.	Density at 60° F.	Viscosity at 20° C.	Ideal Viscosity.	Ratio of Viscosity.	C. P. Hours per Gram.	Per Cent. Error by Curve.
1844	0.7910	0.0168	0.0108	0.643	0.281	0.0
1841	0.8032	0.0197	0.0130	0.660	0.289	0.7
1845	0.7954	0.0155	0.0174	0.735	0.300	0.0
1850	0.7970	0.0162	0.0118	0.729	0.302	0.8
1852	0.7970	0.0159	0.0118	0.743	0.295	1.8
1832	0.7977	0.0146	0.0118	0.809	0.304	4.3
1833	0.7977	0.0142	0.0118	0.830	0.298	2.3
1836	0.7970	0.0136	0.0118	0.868	0.302	1.5
1838	0.7970	0.0135	0.0118	0.874	0.310	1.0
1840	0.7970	0.0144	0.0118	0.820	0.300	1.3
1817	0.7865	0.0168	0.0103	0.614	0.272	0.7
1801	0.7973	0.0125	0.0118	0.945	0.306	1.3
1781	0.7977	0.0123	0.0118	0.964	0.314	0.6
Std. Sample	0.7973	0.0125	0.0118	0.945	0.310	0.0
Kansas	0.8062	0.0167	0.0137	0.821	0.301	1.0
Penn.	0.7852	0.0163	0.0102	0.626	0.266	3.4
Ohio	0.7938	0.0162	0.0117	0.692	0.297	1.3
10	0.8160	0.01851	0.0169	0.913	0.316	3.0
12	0.8139	0.0170	0.0160	0.941	0.311	0.3
3	0.8123	0.0153	0.0155	1.013	0.321	2.5
11	0.7930	0.0166	0.0110	0.663	0.286	0.4
8	0.8153	0.0169	0.0166	0.982	0.301	3.6
1	0.7857	0.0153	0.0102	0.667	0.317	—
2	0.8139	0.0174	0.0160	0.920	0.308	0.4
4	0.8205	0.0201	0.0190	0.945	0.309	0.4
5	0.8139	0.0168	0.0162	0.964	0.310	1.0
13	0.8160	0.0189	0.0169	0.892	0.314	1.8
7	0.7923	0.01652	0.0110	0.665	0.270	6.7
9	0.8092	0.0157	0.0145	0.923	0.309	0.0
6	0.8078	0.0167	0.0140	0.839	0.312	2.0
					Average	1.5

power directly by affecting the flow in the wick. This was tested by changing the temperature of the oil in the vessel. A change of temperature of 18.5° C., affecting the viscosity by 30 per cent., did not produce a change as great as 1 per cent. in the illuminating power.

Take a sample of oil, *e. g.*, number 1844. It has a measured coefficient of viscosity at 20° C. of 0.0168, and its density is 0.7910. Fig. 2 shows that at this density the coefficient of viscosity should be 0.0108. The ratio of the latter to the former is 0.643.

If the above theory is approximately correct we should expect to find that the illuminating power is low. An examination of Table I. shows this to be the case In order to follow this test, I concluded to plot illuminating power and ratio of viscosities, "ideal" to actual, and the result is shown in Fig. 3, the data being taken from Table I.

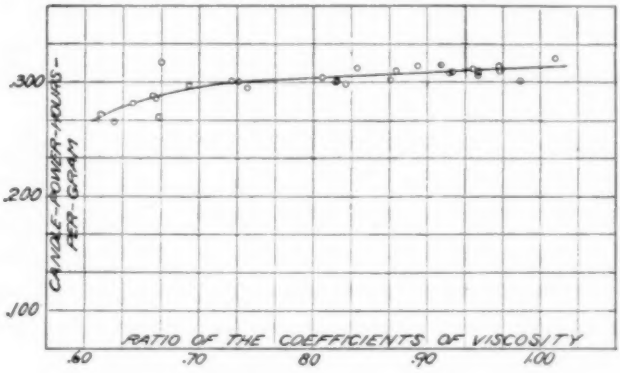


Fig. 3.

(Part of the measurements of density shown in this table were made with a hydrometer. This accounts for the fact that the densities of several samples are exactly the same. The hydrometer was not accurate to the fourth decimal place.) The variations of the observed points from the curve seems to show that the conception involved in the theory above given is at least approximately correct. In fact, as shown by Table I., the average variation in illuminating power when observation is compared with values from the curve is 1.5 per cent. The accuracy of the observations is only 1.0 per cent. The curve therefore presents a very astonishing fact. It shows that it would be possible to compute illuminating power by a measurement of density and viscosity and yet have an error which, on the average, would not exceed 1.5 per cent.

The question at once arises as to whether or not there are limitations to the application of the curve. It is believed that all the

oils used in these experiments had a paraffin base. They were, however, procured from various sources. Numbers 1844 to 1781 were obtained in the market in North Dakota. The oils marked "Kansas," "Penn" and "Ohio" were obtained direct from independent refineries in the states named. The remainder of the samples were procured in the market in Minnesota, South Dakota, Iowa and Missouri. One of the samples is not considered as to percentage variation. It seemed to be quite peculiar in other respects. Even if the curve obtained can with correctness be applied only to oils having a paraffin base, the approximate relation which it shows indicates a decided advance in our knowledge of this subject and suggests the possibilities of a continued investigation by physical methods.

Possibilities of Future Investigations.—The above experiments show conclusively that there are relations between physical quantities which, when ascertained, will be of much service. The greatest value of the approximate relation already shown and described above lies in its promise of reward to the physicist who has the opportunity and the patience to continue an investigation along physical lines.

While illuminating power is an important consideration with burning oils, a subject of more practical importance is that of "burning quality." By "burning quality" is meant the ability of the flame to remain a constant height. The standard of measure is arbitrary. In as much as the character of the oil does not change appreciably with time of burning, it seems entirely possible to explain the variations in burning quality on physical grounds. One of the factors is the clogging of the wick by means of the unvaporized residue; one is the viscosity of the oil; and one is the temperature at the wick producing charring. There are doubtless other factors. An investigation as to the relative importance of these factors would produce gratifying results.

Summary.—This paper contains a report of results obtained by an investigation of kerosene oils by physical methods. It may be summarized as follows:

1. An account is given of preliminary experiments, the results of which were used in correcting observations. The variation of

illuminating power of candle power-hours-per-gram with height of flame, with time of burning, and with different wicks was determined. The temperature variation of the coefficient of viscosity of a good sample of kerosene oil was measured.

2. Distillates of one sample were tested with the results that a relation between illuminating power and density and also a relation between coefficient of viscosity and density were obtained. These results seemed to show that there were present undesirable compounds which affect both the viscosity and the illuminating power.

3. A curve was drawn using observations of illuminating power and ratio of "ideal" to actual coefficients of viscosity. The result of the test with twenty-nine samples obtained from various sources indicates that when the ratio of these coefficients is known the illuminating power can be obtained from the curve with an error, which, on the average, does not exceed 1.5 per cent. This result is probably limited to oils that have a paraffin base.

4. The value of these experiments rests not only in the striking approximate relation thus found, but also in the demonstration of the importance of a study of kerosene oils by physical methods. Attention is called to the problem of ascertaining the relative importance of the physical factors which enter into "burning quality." A continued investigation by physical methods would doubtless produce results of both scientific and practical importance.

THE PHYSICAL LABORATORY,
STATE UNIVERSITY OF IOWA,
June, 1910.

SOME ELECTRICAL PROPERTIES OF SELENIUM.

BY LOUISE S. MCDOWELL.

III. THE INFLUENCE OF TEMPERATURE UPON THE RECOVERY.

IN earlier papers the writer described experiments dealing with the change in conductivity of selenium under the action of light and of X-rays, and in particular with the effect upon the recovery of a variation in the wave-length of the exciting light, the intensity of excitation, and the duration of exposure. In the present paper are described some further experiments to show the change in the resistance of a selenium cell and the form of the resulting recovery curve produced by (1) a sudden increase in temperature; (2) exposure to light at low temperatures.

THE EFFECT OF CHANGE IN TEMPERATURE.

It was early noted that an increase of temperature acts upon selenium as does light to produce an increase in the conductivity. Bidwell from the study of some half dozen cells concluded that for each cell there is a temperature at which the resistance is a maximum and that for the cells studied the temperature of maximum resistance ranged from 14° C. to 30° C.[1] The sensitiveness of the cell towards light has been shown, furthermore, to decrease with an increase in temperature,[2] *i. e.*, to depend upon the resistance.[3] K. Aichi and T. Tanakadate[4] in their study of the influence of temperature upon the electrical conductivity of selenium found that if a cell be warmed and cooled from different temperatures, the conductivity describes a curve without returning to the point of starting and that the final value of the conductivity is higher than the initial value. Pochettino and Trabacchi[5] concluded as a result

[1]Bidwell, Phil. Mag., Vol. 11, p. 302.

[2]R. Marc, Zeits. für anorgan. Chem., Vol. 37, p. 459.

[3]Brown and Stebbins, PHYS. REV., Vol. 26, p. 273.

[4]Aichi and Tanakadate, Tokyo K., Vol. 2, p. 217; Beib., Vol. 29, p. 997.

[5]Pochettino and Trabacchi, N. Cim., Ser. 5, Vol. 13, p. 286.

of many experiments that cells which at ordinary temperatures have a high resistance and decrease in resistance when lighted also decrease in resistance when heated but when cooled do not return to the initial resistance for from twelve to twenty-four hours. Repetition of this changing thermal treatment lowers the resistance and the light sensitiveness and causes the hysteresis to vanish, but after some time the cells resume the original resistance.

In any study of the effect of temperature upon the resistance of selenium it is necessary to distinguish between a change in temperatures possibly not exceeding 100°C. and the effect of prolonged heating at a temperature sufficiently high to bring about an allotropic transformation, which would permanently alter the conductivity and the light sensitiveness. In the present experiments the effect of changes in temperature below 100° C. was considered in order to determine whether the action of light and heat in producing a change in conductivity is the same. If light and heat set up within the cell exactly the same process then the recovery following a return to the initial condition after a sudden increase in light or heat should be of the same type, *i. e.*, the recovery curves should be of the same form.

In the temperature experiments there were used two small home-made cells of the Bidwell type with a sensitive surface about 5×2 cm. in area, mounted by inserting each end in a rectangular block of wood 3×2 cm. in area. The cell thus mounted was enclosed with a calcium chloride drying tube in a tin box just large enough to admit the wooden supports. The terminals were led out through a tube about 20 cm. long, the end of which was plugged with soft wax. The face of the cell so mounted was within about 5 cm. of the wall of the box that it might quickly attain the temperature of the surrounding bath.

The method followed was to plunge the box containing the cell in melting ice and keep it there until the resistance attained a steady value. As in the previous experiments the resistance was measured by making the cell one arm of a Wheatstone bridge balanced for a resistance approximately equal to the mean resistance of the cell and calibrated by the substitution for the cell of known resistances. By this means there was obtained a calibration curve

which gave the resistance of the cell corresponding to any galvanometer deflection. After the resistance at 0° C. had been ascertained the cell was transferred to boiling water and left for periods ranging from ten minutes to two hours until the resistance ceased to decrease appreciably. It was then quickly replaced in the ice-bath and left to

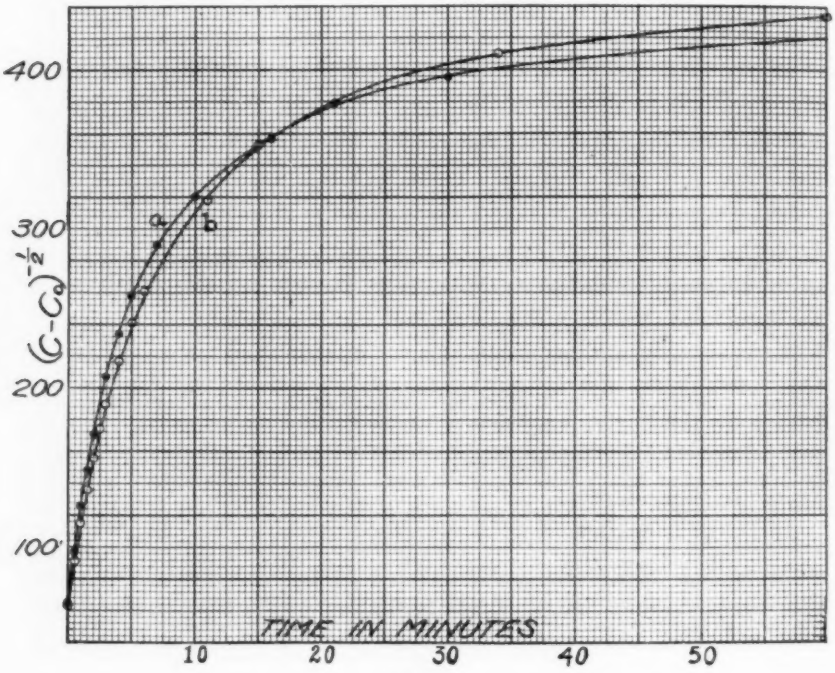


Fig. 1.

Recovery of normal 0° resistance after an increase in temperature of 100°.[1] Cell XVII. Time in 100° bath: *a*, 10 minutes; *b*, 2 hours. Initial 0° resistance: *a*, 103,000; *b*, 97,000.

return to the normal 0° C. resistance. During the recovery the resistance was noted at frequent intervals. From the data so obtained curves were plotted, as in the earlier experiments, with the reciprocal square roots of the changes in conductivity as ordinates and the times as abscissæ. The resulting curves are shown in Figs. 1 and 2. In form the curves are similar to those obtained for the

[1]For these curves additional points were located as follows: *a*, 1°30′, 439, 2°25′, 463, 3°45′, 483; *b*, 1°, 434, 1°30′, 454, 2°, 467.

recovery from excitation by light, with two parts of slight curvature separated by a region of abrupt change of curvature. It is to be noted, however, that in two respects the experiments are not strictly analogous. In the case of recovery from light the contrast was between light and complete darkness, whereas in the case of temperature it is between two temperatures more or less far apart. Furthermore, the return to darkness was almost instantaneous, whereas the temperature change was of necessity gradual. Since the cell required several minutes to attain the temperature of the

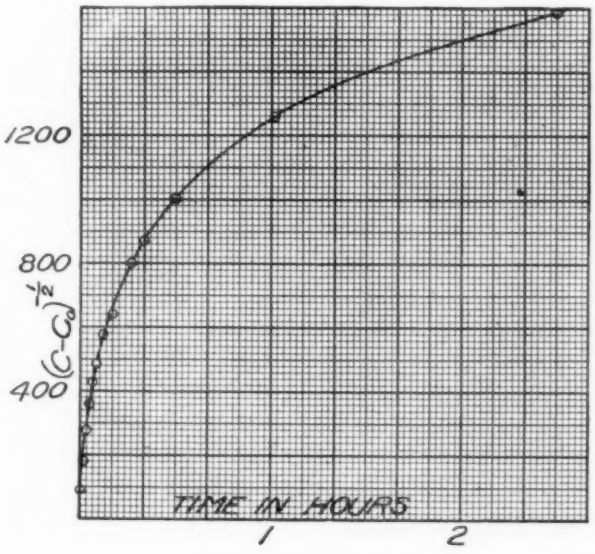


Fig. 2.

Recovery of normal 0° resistance after an increase in temperature of 100°. Cell XVIII. Time in 100° bath, 20 minutes. Initial 0° resistance, 290,000.

bath too great significance cannot be attached to the first part of the curves. It is apparent, however, that heat acts to increase the conductivity in the same way as light. These results partially explain the variation in the normal dark resistance of the cells and also the fact that at a temperature of 100° C. the cells are scarcely at all sensitive to light.

The Action of Light at Low Temperatures.

Since the effect of heat and light upon the selenium cells is the same and the sensitiveness of the cells to light depends upon the resistance, however conditioned, it seems probable that at low temperatures the sensitiveness of the cells would be enormously increased. It was to test this conclusion that the following experiments were undertaken.

The action of light upon selenium at the temperature of liquid air had already been investigated by Pochettino,[1] who found that the dark resistance of his cell decreased from 31,000 ohms at ordinary temperatures to 2,600 ohms at the liquid air temperature while the values of the ratio of the change in resistance to the normal dark resistance were respectively 0.4 and 0.3. Brown and Stebbins,[2] on the contrary, state that the cells used by them were not tested at the liquid air temperature for the reason that the selenium cracked.

In the first of the following experiments comparison was made between the recovery at room temperature, at 0° C., and at the liquid air temperature. Later experiments were made at two intermediate temperatures, about −90° C. and −65° C. For the experiments at the liquid air temperature the cell XVII, used in the temperature experiments, was placed upon a glass plate supported about 2 cm. above the bottom of a glass beaker containing phosphorus pentoxide. The beaker was covered with a thin glass plate sealed with shellac, through which ran the terminal wires. The beaker, enclosed in black paper, was supported by a tight-fitting wooden ring which acted as cover for the Dewar bulb containing liquid air (see Fig. 3). The cell was excited by the light of an acetylene flame placed above the beaker, separated from it by a diaphragm with a circular opening which varied from .6 to 1.2 cm. in diameter and which could be closed by a sliding shutter. This opening could also be covered with a colored glass plate if desired. For the experiments at −90° and −65° the beaker was slipped into a tight-fitting cylinder of tin which extended into

[1] Pochettino, Rend. R. Accad. dei Linc., Ser. 5, Vol. 11, 1 Sem., p. 286.

[2] Brown and Stebbins, Phys. Rev., Vol. 26, p. 273.

the liquid air. The temperature was regulated by the distance the beaker fitted into the cylinder and by the distance the cylinder dipped into the liquid air. By this means the temperature of the cell could be kept constant within 5° or 10° as indicated by a thermometer sealed in through a hole in the glass plate covering the beaker. As the thermometer was found to be unreliable for temperatures below −100° no readings were secured between that temperature and the liquid air temperature. In no case was the cell excited without a rest of at least twenty-four hours in the dark. For the experiments at ordinary temperatures the same apparatus was used, that the conditions might be as nearly uniform as possible.

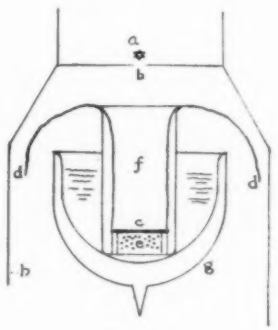


Fig. 3.

a, Acetylene flame; *b*, circular aperture; *c*, cell; *d*, terminal wires; *e*, phosphorus pentoxide; *f*, beaker; *g*, Dewar bulb; *h*, screens.

The method followed was to lower the cell into the liquid air and leave it from thirty minutes to four hours before excitation. Sometimes the cell was left on open circuit and sometimes on closed circuit, with no apparent effect on the results. The resistance of the cell was found to increase so enormously as to be entirely beyond the range of calibration of the bridge. Hence in the later experiments the resistance was measured roughly by balancing the Wheatstone bridge. That this method was far from accurate is evident from the following figures which give the values of the resistances in the three arms of the bridge and the calculated resistance of the cell in a typical instance.

500,000 : 200 = x : 100,000	x = 250 megohms.
1,000,000 : 480 = x : 200,000	x = 417 "
500,000 : 130 = x : 100,000	x = 385 "
1,000,000 : 240 = x : 100,000	x = 417 "
250,000 : 80 = x : 80,000	x = 250 "

While these results differ widely it is to be noted that they are of the same order of magnitude and from the method of plotting it is evident that the curves would not depart appreciably from the correct form if the resistance were assumed to be infinite.

After the cell had been thus cooled and its resistance measured it was excited in the manner already indicated for 10 sec. in the earlier experiments and for a time sufficient to produce saturation

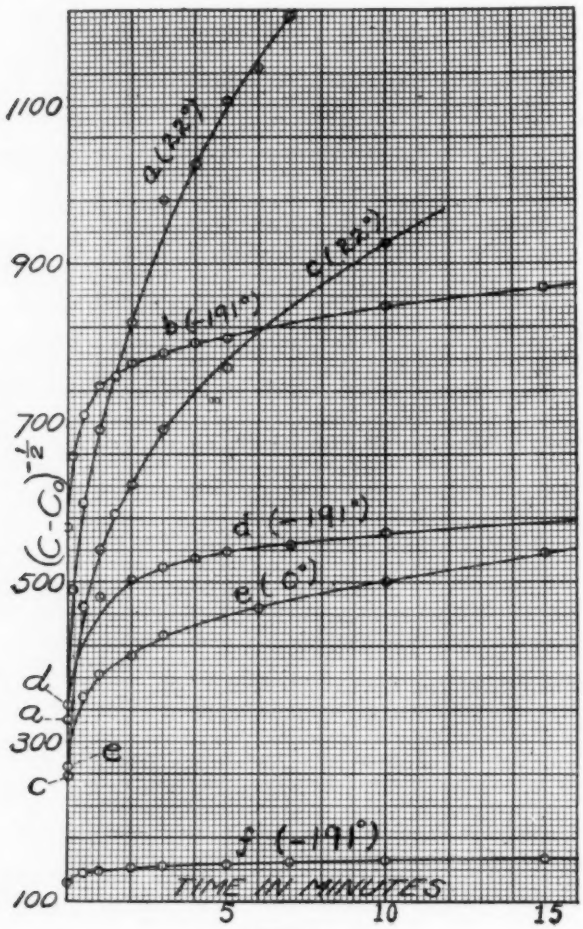


Fig. 4.

Variation in rate of recovery from excitation by light at different temperatures and intensities. Cell XVII. Red light excitation, *a*, Diameter of aperture, 0.6 cm.; time of excitation, 10 sec.; initial dark resistance, 64,000 ohms; *b*, diameter of aperture 0.6 cm., time of excitation 10 sec., initial dark resistance 4×10^8 ohms;[1] *c*, diameter of aperture 0.9 cm., time of excitation 10 sec., initial dark resistance 71,700 ohms; *d*, diameter of aperture 0.9 cm., time of excitation 10 sec., initial dark resistance 4×10^8 ohms;[1] *e*, diameter of aperture 0.6 cm., time of excitation, to saturation, initial dark resistance 92,500 ohms; *f*, diameter of aperture 0.6 cm., time of excitation, to saturation, initial dark resistance 4×10^8 ohms.

[1]Resistance assumed from later experiments with this cell.

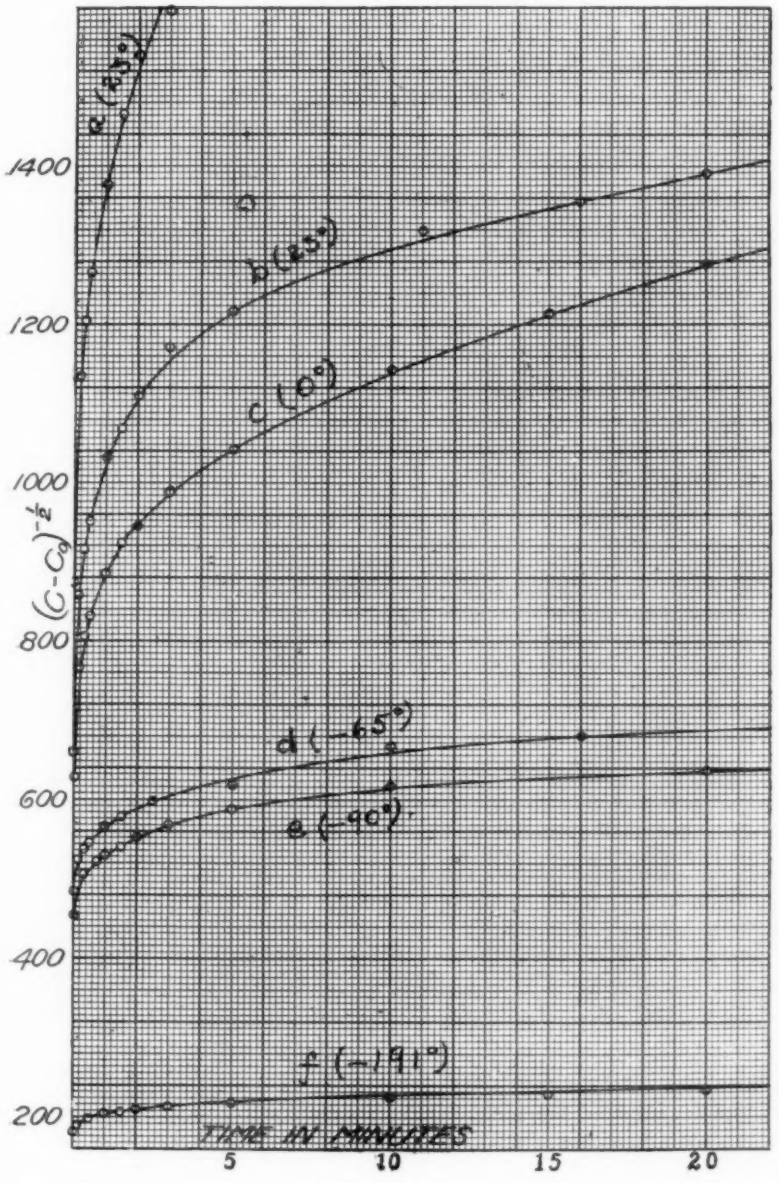


Fig. 5.

Variation in rate of recovery from excitation by light at different temperatures. Excitation to saturation. *a*, *d*, *e*, Cell XXI.; white light through aperture 0.9 cm. in diam.; initial dark resistances: 292,000; 3.6×10^6; 9×10^6. *b*, *c*, *f*, Cell XIX.; red light excitation, aperture 0.6 cm.; initial dark resistances: 209,500; 417,000; 2×10^9.

in the later experiments. The instant the light was turned on the resistance began to decrease at so extremely rapid a rate that for the first few seconds it was impossible to follow the change by the galvanometer method used. By the time approximate saturation was reached in one or two hours the resistance had fallen to only

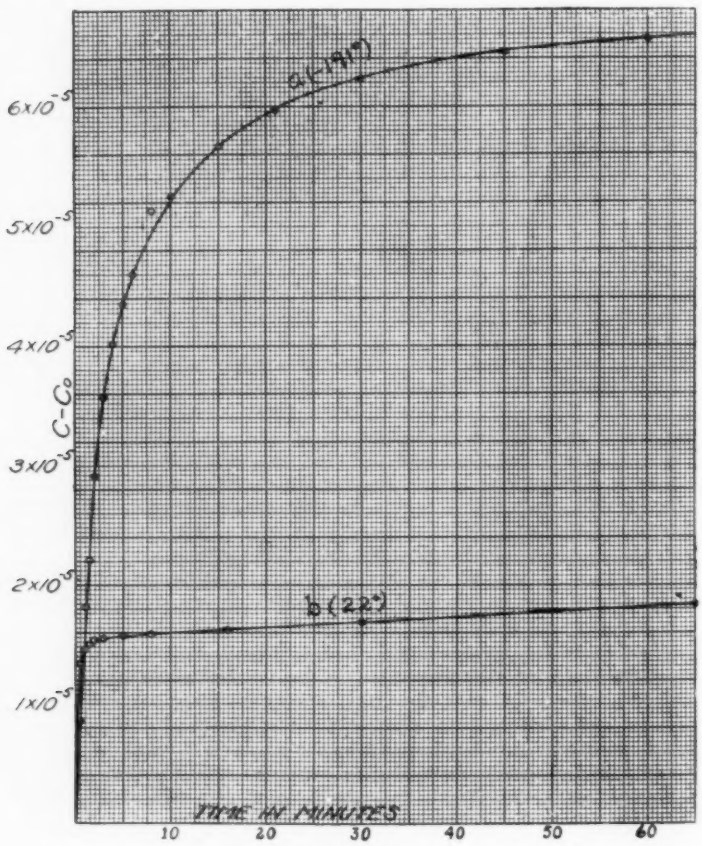


Fig. 6.

Variation in rate of saturation at different temperatures. Cell XVII. Excitation by red light through aperture 0.6 cm. in diam. Initial dark resistances: *a*, 4×10^{8}; *b*, 40,600.

a few thousand ohms. The circular opening for the admission of light was then closed and the cell left to recover the normal dark resistance. At frequent intervals the resistance was noted. Re-

covery was found to be extremely slow and in no instance was it found practicable to prolong the experiment sufficiently to bring the resistance of the cell anywhere nearly back to the value before

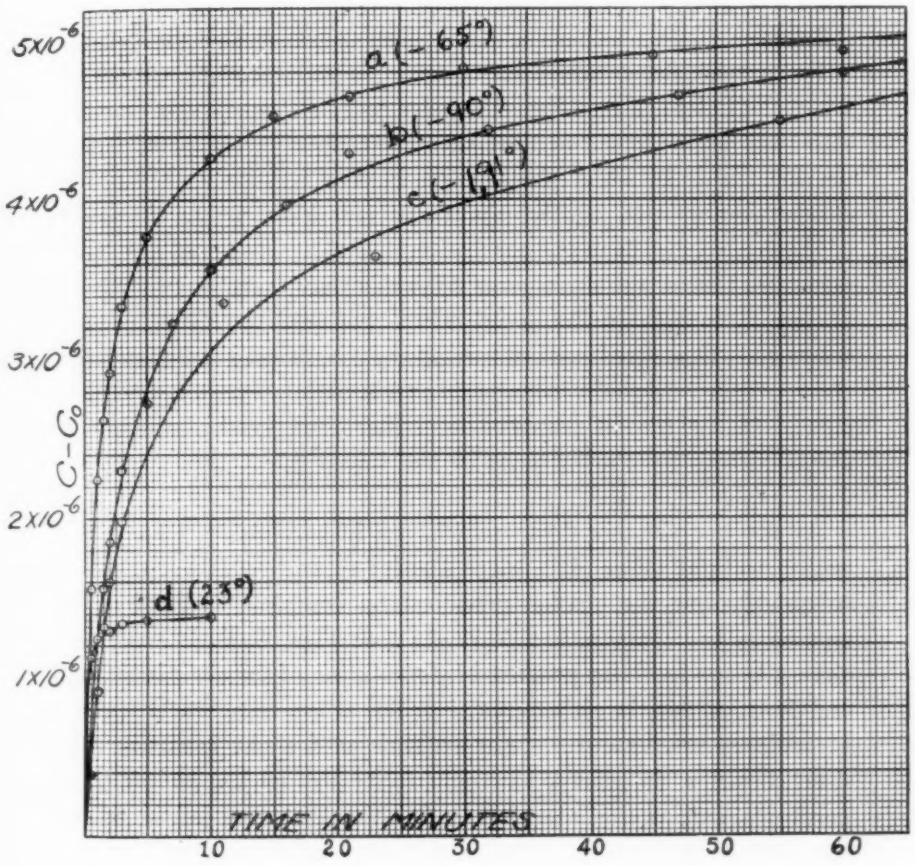


Fig. 7.

Variation in rate of saturation at different temperatures.[1] Cell XXI. Excitation by white light through aperture 0.9 cm. in diam. Initial dark resistances: *a*, 3.6×10^6; *b*, 9×10^6; *c*, 6×10^7; *d*, 292,000.

[1]Additional points were located as follows:

a, 1°15′, .000005041; *b*, 1°15′, .000004991; *c*, 1°13′, .000004791. It is to be noted that the curves extend very nearly to a point where the lower curves would cross the upper, thus indicating the probability that the change produced by saturation increases with decrease in temperature even at temperatures approaching that of liquid air.

excitation. Twenty-four hours after the conclusion of the experiment the dark resistance of the cell at room temperature was found to be somewhat higher than before the experiment. For the experiments at other temperatures the same method was followed.

From the data obtained there were plotted recovery curves in which, as before, the reciprocal square roots of the changes in conductivity were plotted against the times (see Figs. 4–5) and saturation curves in which the changes in conductivity during excitation were plotted against the times (see Figs. 6–7). A study of these curves leads to the conclusion that the recovery at low temperatures follows the same general laws as that at ordinary temperatures. The greater the initial effect produced the slower is the recovery. Compared with the recovery at ordinary temperatures the recovery at liquid air temperatures is extremely slow, and this change in the rate of recovery is greater than would be brought about merely by the increase in the initial effect produced (see Figs. 4–5).

As the temperature decreases change in conductivity upon exposure to light takes place more slowly; saturation is not reached so quickly but the change produced by complete saturation increases as the temperature decreases (see Figs. 6–7). Hence the change in conductivity produced by excitation of the same intensity and duration may be either greater or less at low temperatures than at ordinary temperatures. For excitations of slight intensity and short duration the change in conductivity will be less at low temperatures, but as the intensity or duration of excitation increases the ratio of the change at liquid air temperature to that at room temperature increases. The values of this ratio for the initial points of curves *a* and *b*, *c* and *d*, *e* and *f*, Fig. 4, are respectively 33 per cent., 56 per cent. and 476 per cent. Furthermore, since the initial dark conductivity at liquid air temperature is so nearly zero the ratio of change in conductivity to the initial conductivity is enormously greater than at ordinary temperatures.

Summary.

The results of the investigation may be briefly summarized as follows:

1. The action of light and heat in producing change in the conductivity of selenium is apparently identical.

2. The increase in resistance with decrease in temperature continues down to the temperature of liquid air where the cell becomes almost entirely non-conducting.

3. Change in conductivity due to excitation by light of the same intensity takes place more slowly at low temperatures than at ordinary temperatures, but the final change produced by saturation is enormously greater.

4. Recovery at low temperatures is markedly slower than at ordinary temperatures.

This investigation was carried out during the summer of 1909 in the Physics Laboratory of Cornell University, and in conclusion the writer desires to express her thanks to Professors Merritt and Shearer for their many helpful suggestions.

WELLESLEY COLLEGE.

ON THE INITIAL VELOCITY OF ELECTRONS AS A FUNCTION OF THE WAVE-LENGTH IN THE PHOTOELECTRIC EFFECT.

BY JAKOB KUNZ.

THE photoelectric effect is bound to throw a considerable amount of light upon the phenomena of radiation. It is characteristic of most modern theories of radiation that the electromagnetic energy is divided up into elements or units, which are emitted individually by a source of light and absorbed also individually by an absorbing substance. These theories seem to make a compromise between the classic wave theory of light and the emission theory of light. The principle of relativity appears to support this newest view of the electromagnetic energy. Indeed, if the equations by means of which the laws of the phenomena of nature are expressed are independent of the system of coördinates, it is immaterial whether we coördinate an independent medium like ether to the system of coördinates at rest in motion. In other words an independent medium like ether is superfluous from the standpoint of the principle of relativity. In addition, the electromagnetic energy in the theory of relativity appears in the form of physical or material entities, always connected with a certain amount of mass.

$$dE = dm \times C^2.$$

The properties of the electromagnetic units of energy are unknown. In Planck's theory of radiation an oscillator absorbs and emits the electromagnetic energy not continuously but in definite amounts such that the element of electromagnetic energy is equal to $E_1 = hn$ where $h = 6,\ 5.10^{27}$ and n the frequency of the light absorbed or emitted. I have shown in a recent article[1] that the electron theory of radiation leads to the result that the energy in a simple harmonic wave is proportional to the square of the frequency,

[1]Jakob Kunz, On the Photoelectric Effect and its Bearing on the Structure of the Ether. PHYS. REV., Vol. XXIX., p. 212, 1909.

$E = kn^2$. If the vibrating electrons were to emit the energy not continuously over the wave front, but only in certain directions, and if the laws of the electromagnetic field apply to these special directions in the same form as for the electromagnetic field, then we could draw the conclusion that the electromagnetic energy for each monochromatic beam remains constant as it travels on through space, being proportional to the square of the frequency. This point of view can be tested in different ways. Perhaps the most direct way of finding an answer to the problem before us is given by the photoelectric effect. In the preliminary experiments the accuracy was not sufficiently great to decide between the two possibilities.

In order to work with a very definite surface, to avoid the productions of electrons due to reflected light on the platinum cathode and to have as large an interval of wave-length as possible, the alkali metals lend themselves to the measurements required in the first place.

The apparatus and method adopted have already been described. It was found more convenient to keep the tube containing the liquid sodium potassium alloy in a given position and to rotate the prism so that the beams of various colors acted on the liquid alloy. The spectrum was calibrated by means of the lines of mercury, sodium and lithium arcs. The Dolezalek electrometer had a very high degree of sensitiveness. The quartz suspension was made a conductor by means of calcium chloride solution and the deflection due to a potential difference of 1 volt between the quadrants was about 140 mm., when the needle was kept in connection with a battery of 6 volts whose second terminal was connected to earth. The sensitiveness remained absolutely constant for any required length of time. The electrometer was calibrated several times during the progress of the experiment. The deflection-potential curve was very nearly a straight line.

In order to get the electrical insulation as perfect as possible, many efforts were made to supply a tube of the type of Fig. 5, of the above-mentioned article where the platinum wire connecting the sodium potassium alloy with the electrometer was insulated from the glass by means of amber. Various kinds of sealing wax

and Kotinsky cement were used, but the vacuum could not be maintained to the degree required, and the surface of the alloy began to be contaminated by the oxides after about a day. I was therefore finally obliged to work with a tube of the form shown in Fig. 6. The insulation was not as satisfactory as in the previous tube, but the vacuum remained constant for over four months. The metals were introduced in the tube which was filled with nitrogen, the tube sealed off, the vacuum established, the metals melted and partially distilled in the second part of the tube. The whole system of tubes was heated as high as the vacuum would allow; this heating operation being repeated several times and the tube finally separated from the pump. The metal was allowed to flow through the glass funnels into the final position. It was very strongly active.

Two methods were adopted for the determination of the maximum initial velocities of the electrons. One way consisted in measuring the maximum positive potential acquired by the alloy under the action of a beam of given wave-length. This method involves a certain error due to incomplete insulation. The maximum deflection was about 210 mm., and the leak amounted to 4 or 5 mm. scale divisions per minute. Eight deflections were taken for each wave-length. A series of readings were taken from the violet end of the spectrum, towards the red end and repeated in the opposite direction. A complete series required about three hours. The two sets of readings corresponding to the two movements coincide exactly. The observations were continued for about three months; during this time interval the only change observed in the initial velocities was an exceedingly small decrease. The red end of the spectrum requires a special study; it has been found that in this region the initial velocity of the electrons increases with increasing wave-length, whereas from the violet to the yellow end of the spectrum, it decreases regularly and continuously. A small electromotive force opposite in direction to the E.M.F. of the photo-electric effect was acting very slowly. The nature of this force is still unknown; it has made accurate measurements with potassium and rubidium amalgam so far impossible. In these amalgams the negative electromotive force amounted to about 5 volts, and produced a very sudden deflection of the electrometer, as soon as

connection with the cell was established. A bulb of charcoal was connected with the tube containing the sodium potassium alloy. The results of the readings were the same whether the bulb was surrounded by liquid air or not. The following table contains the

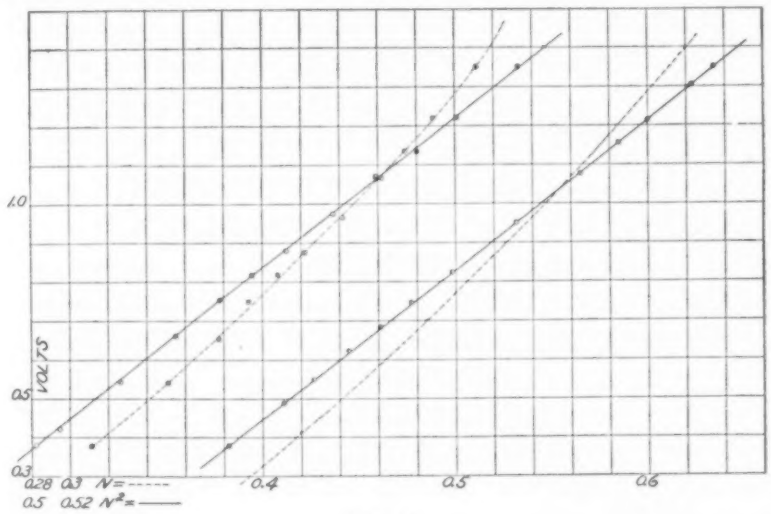


Fig. 1.

results of two series of measurements; they are plotted in Fig. 1 where the volts are the ordinates and n^2 the abscissæ for the straight line and n the abscissæ for the dotted curve representing the parabola.

n	n^2	Volt.	n	n^2	Volt.
0.5302	0.282	0.38	0.532	0.283	0.38
0.542	0.294	0.426	0.542	0.294	0.428
0.572	0.326	0.549	0.557	0.311	0.49
0.5965	0.355	0.66	0.571	0.326	0.55
0.613	0.377	0.76	0.587	0.345	0.62
0.628	0.395	0.82	0.601	0.361	0.682
0.642	0.412	0.88	0.614	0.377	0.742
0.662	0.4375	0.975	0.631	0.398	0.824
0.679	0.461	1.07	0.6425	0.413	0.88
0.693	0.480	1.14	0.657	0.432	0.955
0.7076	0.5005	1.22	0.674	0.454	1.04
0.731	0.533	1.35	0.681	0.464	1.08
			0.697	0.485	1.16
			0.707	0.500	1.21
			0.7225	0.522	1.31
			0.731	0.534	1.35

It appears that the potential difference acquired by the potassium-sodium alloy is proportional to the square of the frequency of the light. Let us express this connection by the equation:

$$v = an^2 + b,$$

$$a = \frac{v_1 - v_2.}{n_1^2 - n_2^2.}$$

Let us take the following values from the curves:

$v_1 = 1.31$, $\qquad n_1^2 = 0.522 \times 10^{30}$,

$v_2 = 0.38$, $\qquad n_2^2 = 0.282 \times 10^{30}$.

$$a = 3.86 \times 10^{-30} \frac{volts}{n^2},$$

or

$$a = 1.16 \times 10^{-27} \frac{absolute\ units\ of\ v}{n^2},$$

$b = v_1 - an_1^2 = -0.715$ volt, $= v_2 - an_2^2 = -0.714$ volt.

The constant b measures the work required to drag an electron out of the sodium-potassium alloy.

$$b = \frac{0.714}{300} = 0.00238 \text{ absolute units.}$$

$$e \times v = 4.65 \times 10^{-10},\ 2.38 \times 10^{-3} = 1.11 \times 10^{-12} \text{ ergs.}$$

We know, on the other hand, that the work required to produce an an ion by α particles in a gas is equal to 4.4×10^{-11} ergs.

In this way the photoelectric effect affords a means of measuring the work required to drag an electron out of a metal. That this work must be considerable has recently been shown by W. W. Williams in an article published in this journal; indeed the spark discharge between metal plates at a very short distance shows that an electric force of 300 volts acting over a distance of about 1 wavelength of sodium light is unable to drag the electrons out of the metal. This gives a lower limit of the force and energy necessary to produce an electron.

We are here certainly dealing with surface forces and we should therefore expect that the constant b depends very largely on the conditions of the surface layer of the metal.

The second method of measuring the initial velocity of the electrons consists in applying a variable retarding potential and determining the current between the two electrodes. It was necessary to shunt a condensor parallel to the electrometer in order to get a deflection sufficiently slow. If there were only one type of electrons, escaping with the maximum velocity, and if we apply a variable potential to the sodium-potassium alloy, we should expect to find a certain current, until the potential passing through zero becomes positive and when it requires that value which is just sufficient to prevent the electrons from escaping, then the current should suddenly from the constant value drop down to zero and remain zero, if the positive potential is increased. If, however, there are electrons escaping with various velocities, then we should expect a curve of the type given in Fig. 2, which shows that there are indeed

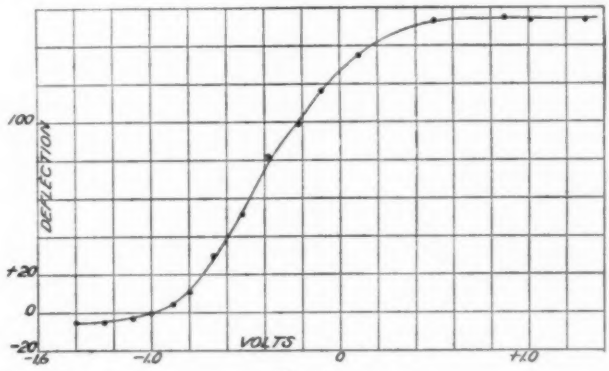


Fig. 2.

many electrons escaping with velocities different from the maximum velocity. The volts applied and the corresponding deflections observed are given in the following table:

Volts.	Deflections.	Volts.	Deflections.
−1.6	− 4	−0.37	+81.2
−1.4	− 4	−0.08	108.3
−1.2	− 3.5	+0.1	118.0
−1.1	− 2.0	+0.3	154.0
−1.0	− 0.4	+0.88	153.5
−0.88	+ 6.6	+1.0	154.2
−0.68	+29.5	+1.6	154.4

It was easy to correct the curve thus obtained for the leak between the electrodes. The corrected curve still shows a tendency to fall under the axis of abscissæ, so that the potential which prevents the electrons from escaping, cannot be determined with absolute accuracy and the error involved in this method is not much smaller than the error involved in the first method. The wave-length was 451 mm., $n = 0.666$, the voltage observed is 1.01 and according to the first method equal to 1.02. There is a little irregularity in the last curve, which was more pronounced in the curves obtained with higher frequency. In a previous paper published in this journal it has been found that the plane of polarization has a certain though small influence on the positive potential acquired. The experiment repeated showed the same effect, but the difference in the potential due to the two positions of the plane of polarization with respect to the plane of incidence appeared to be somewhat smaller than before.

While I was working in the visible part of the spectrum, Albert W. Hull[1] studied the initial velocities of the electrons emitted from carbon under the action of ultra-violet light in interval from $\lambda = 171-$ to 123 mm.

The general result of his research agrees well with the results obtained above showing that the positive potential of the substance acquired under the action of light is proportional to the square of the frequency.

If we represent these results by the equation

$$v = an^2 + b,$$

we find for

$v_1 = 3.03,$ $\lambda_1 = 123,$ $n_1^2 = 5.96 \times 10^{30},$

$v_2 = 1.57,$ $\lambda_2 = 171,$ $n_2^2 = 3.07 \times 10^{30},$

$$a = \frac{v_1 - v_2}{n_1^2 - n_2^2} = 0.506 \times 10^{-30} \frac{\text{volt}}{n^2},$$

$$a = 1.52 \times 10^{-28} \frac{\text{absolute units}}{n^2},$$

[1]Albert W. Hull, Die Anfange geschwindig keiten der durch ultraviolettes Licht-erzeugten Elektronen, Physikalische Zeitschrift, Vol. 10, p. 537, 1909.

a value which is considerably smaller than that obtained with sodium-potassium alloy. For the constant b we get:

$$b = 0.02 \text{ volt.}$$

Thus the straight line: positive potential divided by the square of the frequency seems to pass through the origin of the system of coördinates, or the work required to drag an electron out of carbon is very small in comparison with that calculated for sodium potassium alloy.

The first experiments on the subject under consideration have been carried out by E. Ladenburg,[1] who drew the same conclusions from his results; namely, that the positive potential acquired by platinum, copper and zinc is proportional to the square of the frequency of the ultraviolet light.

From his figures I deduced the following values of the constants a and b:

Platinum,	$a = 2.47 \times 10^{-28}$	$b = 0.12$ volts
Copper,	$a = 2.28 \times 10^{-28}$	$b = 0.01$ volts
Zinc,	$a = 1.38 \times 10^{-28}$	$b = 0.02$ volts

These values agree much better with those obtained by Hull than with those found by myself. But it is remarkable that the values of the positive potentials given by Ladenburg and Hull are very small in comparison with those obtained with sodium potassium alloy. Thus Ladenburg gives for $\lambda = 201$ mm., a positive potential of zinc 1.12 volts while I find for $\lambda = 409$ mm., a positive potential of sodium potassium alloy equal to 1.34 volts.

It has been shown by A. Ioffe[2] that Ladenburg's observations admit of an interpretation in favor of Planck's theory of radiation, *i. e.*, that the positive potential of the three metals increases directly as the frequency of the ultraviolet light. In Hull's experiments however, and in my own results this interpretation is impossible. The problem can only be solved by making measurements through the whole range of the visible and ultraviolet spectrum. In the present most of the results obtained seem to be in favor of that theory which requires the energy of a simply harmonic wave motion

[1] E. Ladenburg, Physikalische Zeitschrift, Vol. 8, p. 590, 1907.

[2] A. Ioffè, Annalen der Physik, XXIV., p. 939, 1907.

to be proportional to the square of the frequency. In conclusion I wish to call attention to the remarkable fact that R. A. Millikan has found that for several metals under powerful illumination continued intermittently for several weeks the positive potential gradually rose to a vlaue ten and even thirty times larger than the initial value.

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SOME CALORIMETRIC METHODS.

By Walter P. White.

THE calorimetric method of mixtures has recently undergone a marked development. New methods have been introduced, and the standard of accuracy has been greatly advanced. The significance of this development is not yet wholly clear; considerable disagreement is manifest as to the exact relation between the methods and the accuracy, so that the value of the methods and the relative importance of the remaining sources of error are still uncertain.

The present series of papers makes some contribution toward a further knowledge of the different calorimetric errors and of the advantages of different methods. It also describes some apparatus and methods now in use at the Geophysical Laboratory, of which some account has already been given.[1]

1. A Short Method for Getting the Cooling Correction.

The cooling correction is often discussed with the aid of a figure[2] similar to Fig. 1, where the heavy curve represents the calorimeter temperature, plotted against time. If heat is communicated to the calorimeter during the *transfer period*, 1, raising the temperature from ϑ_0 to ϑ_2, some heat will (usually) at the same time be lost by convection, etc. The heat transferred will thus be measured by the temperature difference, $\vartheta_2 - \vartheta_0$, plus the loss of temperature due to the heat which has escaped. This loss is the cooling correction. It has to be calculated, and the data required are, first, the temperatures of the calorimeter during the transfer period, and second, the relation between these temperatures and the cooling

[1]Walter P. White, Phys. Rev., *25*, 137, 1907; *26*, 536, 1908; *28*, 461, 1909; Amer. Journ. Sci. (4), *28*, 334, 1909.

[2]The essentials of which, as well as some other features of the present discussion were suggested by the paper of Jaeger and von Steinwehr, Ann. d. Phys., *21*, 23, 1906.

rate. This relation varies from time to time, and is usually redetermined for each experiment.[1]

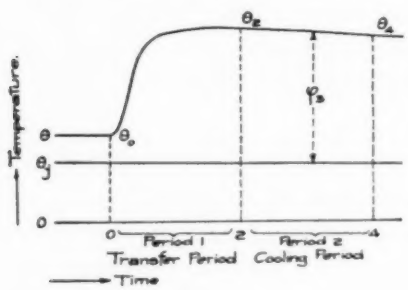

Fig. 1.

Temperature-time diagram of a typical calorimetric determination.

The most advantageous method of getting the cooling correction will depend somewhat upon the experimental conditions. A very simple (and probably new) procedure is possible if the enviroming temperature can be measured, and if the heat change due to stirring and evaporation is known to a rough approximation. In deriving the formula, it will[2] be convenient to put:

ϕ_n for the temperature difference of calorimeter and jacket at the time, t_n,

$\Phi_m = \int_m \phi$, for the total value of φ for the interval T_m,

w, for the temperature fall per minute due to the combined effect of evaporation and stirring.

The value of the cooling rate for any particular experiment is found by running a cooling period immedately after the transfer period. During this period the temperature falls from ϑ_2 to ϑ_4. The value of Φ is then Φ_3, for which T_3 times the mean value of

[1]Some observers have also redetermined it for several different temperatures in each case, as if by so doing greater accuracy could be obtained. This does not appear to be true for the experimental conditions contemplated in the present paper. The change of the cooling rate with temperature is so nearly linear that its deviation from proportionality is commonly neglected (data on this point are given on p. 556); the variation of this negligible variation can hardly compare with the changes which may result from the manipulation and delay of the supposedly more accurate procedure. See further, p. 550, footnote 2.

[2]Notation. The notation here used agrees with that of most writers on this subject in using V for rate of cooling. It agrees with Jaeger and von Steinwehr in taking t for time, with Pfaundler and with Louguinine and Schukarew in using ϑ for temperature, though it differs from them in doing so consistently. Primes indicate corrected quantities; subscripts refer only to time, odd numbers for the periods, even, for their terminations. The additional symbol, ϕ, is introduced for the temperature difference of calorimeter and jacket, with Φ for its integral. w indicates that part of the rate due to stirring and evaporation.

ϕ can always be taken. The experimental data required, then, are (besides the time intervals, T_1 and T_3) the temperatures, ϑ_0, ϑ_2, ϑ_4, the integrated differential temperatures Φ_1, and Φ_3, and, approximately, the rate w. It will be convenient to begin by assuming that the heat *directly* lost is proportional to φ; that is, that Newton's law of cooling holds. This assumption underlies most cooling correction methods. Here it is made merely to simplify the presentation, and will be dispensed with presently. In accordance with this assumption, since

$$\vartheta_2-\vartheta_4-wT_3 \tag{1}$$

is the *direct* loss of temperature in period 3,

$$(\vartheta_2-\vartheta_4-wT_3)\frac{\Phi_1}{\Phi_3} \tag{2}$$

is that in period 1, and

$$(\vartheta_2-\vartheta_4-wT_3)\frac{\Phi_1}{\Phi_3}+wT_1 \tag{3}$$

is the cooling correction. The advantage of this formula is gained by transforming it through

$$(\vartheta_2-\vartheta_4-wT_3)\left(1+\frac{\Phi_1-\Phi_3}{\Phi_3}\right)+wT_1 \tag{4}$$

to

$$\vartheta_2-\vartheta_4+(\vartheta_2-\vartheta_4-wT_3)\frac{\Phi_1-\Phi_3}{\Phi_3}+w(T_1-T_3). \tag{5}$$

Here the first two terms are directly observed; the fourth vanishes if $T_1 = T_3$, that is, if the two periods are taken of equal length; the third becomes very small if Φ_1 is nearly equal to Φ_3. Now in many cases Φ_1 can be nearly equal to Φ_3 when T_1 equals T_3. Hence in such cases a very imperfect knowledge of w suffices, and the computation of the second term can always be done by the slide rule, and often by inspection. Another advantage of the method lies in the fact that it is wholly independent of all conditions previous to the time, t, the beginning of the transfer period. Hence the method is of value whenever it is desirable to alter the constants of either calorimeter or jacket at that time (as by dropping bodies in, putting on a cover previously left off for convenience, etc.), since it

imposes no restrictions whatever on such operations, and requires no correction or allowance for the change produced.

2. THE CUSTOMARY METHOD.

The fundamental requirement of the previous method, that the temperature of the environment shall be measured, is incompatible with most existing apparatus, where the jacket does not cover the calorimeter, and the environment consists of various bodies, at different temperatures. For this state of affairs the ordinary Regnault-Pfaundler method is adapted, in which observations on an additional cooling period give data enough for eliminating not only the effect of the environing temperature, but also that of the stirring, etc. This method, however, does require that the environing temperature be assumed to be constant, that no changes take place in the calorimeter constants,[1] and that Newton's law holds.[2] In order to make this last assumption true, it is customary to limit the temperature range used, often to less than 2°.

The formula for this method seems to admit of a simpler derivation than has yet been offered. To obtain it, let V be put, as usual, for the *observed* cooling rate, $= d\vartheta/dt$. Let K be the cooling constant of the calorimeter, let ϑ_e be the mean effective temperature of the environment, and let the subscript -1 indicate the quantities belonging to the extra cooling period (which comes before the time denoted by zero in Fig. 1). Then $V - w$, the direct cooling, $= K(\vartheta - \vartheta_e)$,

or

$$K = \frac{V - w}{\vartheta - \vartheta_e} \tag{6}$$

W and ϑ_e are, of course, unknown. The extra cooling period renders it possible to eliminate them, for, by composition of ratios,

$$K = \frac{V_3 - V_{-1}}{\vartheta_3 - \vartheta_{-1}}, \quad = \frac{V_x - V_{-1}}{\vartheta_x - \vartheta_{-1}}, \text{ etc.}, \tag{7}$$

and therefore

$$V_x = V_{-1} + K(\vartheta_x - \vartheta_{-1}), \quad = V_{-1} + \frac{V_3 - V_{-1}}{\vartheta_3 - \vartheta_{-1}}(\vartheta_x - \vartheta_{-1}), \tag{8}$$

[1]Such as are produced by dropping bodies in, etc. When they occur, further corrections are necessary.

[2]For data on the importance of this assumption, see p. 556.

where V_x is the unknown rate corresponding to any observed temperature, ϑ_x, and the other ϑ's are the *mean* temperatures of the intervals indicated by their subscripts. In this formula, ϑ_{-1} replaces ϑ_e as the temperature of reference, the difference between V_{-1} and any rate being proportional to the difference between ϑ_{-1} and the corresponding temperature. The cooling correction can now be expressed at once. It is merely the integral of V_x for the transfer period, or

$$V_{-1}T_1 + \frac{V_3 - V_{-1}}{\vartheta_3 - \vartheta_{-1}}\left[\int \vartheta dt - \vartheta_{-1}T_1\right]. \qquad (9)$$

This is essentially Pfaundler's formula.[1]

3. The Surrounding Temperature.

The two methods just presented are alike in requiring that the heat of stirring and evaporation shall be constant.[2] The environing temperature must be known for the first, but need not be constant; for the second it must be constant, but need not be known. The probable amount of error from a failure of constancy (in case the second or Regnault method is used) can be easily estimated by considering a simple case. Suppose the calorimeter temperature rises suddenly at first and then remains sensibly constant through both the transfer and the cooling period. Suppose the two periods

[1]Jaeger and von Steinwehr's final formula (4) differs from this only in leaving the whole bracketed term for graphic integration, and in substituting

$$\frac{\vartheta_2 - \vartheta_0}{2} + \frac{1}{2K}(V_0 + V_2)$$

(afterward multiplied by K) for V_{-1} in the first term. In copying Pfaundler's formula, however, and in stating their own, Jaeger and von Steinwehr, though using values of V taken over the two cooling periods (*i. e.*, V_{-1} and V_3), number these as if they applied to the end temperatures (*i. e.*, V_0 and V_2 in the present notation), and hence are led to insert, instead of ϑ_{-1} and ϑ_3, the end temperatures ϑ_0 and ϑ_2, which do not correspond to the V's as actually determined. But $\vartheta_2 - \vartheta_0$ may differ from $\vartheta_3 - \vartheta_{-1}$ by $KT_3/2$ of itself, and this error will affect the cooling correction proportionately. The resulting final error, while safely negligible in their case, will often exceed .0005 of the whole temperature ri e, or about the usual magnitude of the thermometer lag error (pointed out by Jaeger and von Steinwehr) which has in two instances been accounted an important reason for the introduction of new calorimetric methods. Of course, it is just as easy to use the correct values, ϑ_{-1} and ϑ_3.

[2]That it must also be approximately known for the first method practically adds nothing to the difficulty of the method.

are equal in length. The Regnault method will then make the cooling correction, that is, the loss in the transfer period, equal to the loss in the cooling period, because the temperatures of the two are equal. But if the environing temperature changes, the temperature difference, on which the cooling depends, will not be the same, and the error will be proportional to the change in the environment from one period to the other. For instance, a fair value of the cooling correction is 25 per mille of the total rise, so that for an accuracy of 1 per mille the correction must be known to one twenty-fifth. If, then, the rise is 2.5°, an accuracy of 1 per mille requires an environment constant to 0.1°, while to reach 0.1 per mille, an accuracy already attained in this type of calorimetry,[1] an environment constant to .01° is needed.[2] With a more gradual rise of the calorimeter temperature, the error becomes less, but in very many cases it will be at least half that just given. It is clear that the simplest solution of the difficulty will often be to provide an environing temperature which can be measured, and which, therefore, does not need to be constant. This will usually call for: (1) a stirred water jacket, completely inclosing the calorimeter; (2) the absence inside it of all bodies at indefinite temperatures, such as calorimeter covers not touching the water of the calorimeter. The fulfillment of these two requirements gives a system in which practically everything is at one of two measured temperatures, where the direct heat loss from the calorimeter, the cooling proper, is so regular as to be practically negligible as a source of error.

The complete jacket has sometimes been condemned[3] on account of the irregularity it may introduce into the evaporation, which will vary as the confined space approaches saturation. Irregular evaporation is a serious source of error, but the remedy thus suggested, of exposing the calorimeter to the whole room, and then, perhaps, restricting ventilation, burners and lights, in order to keep the room in a constant condition,[4] seems rather crude, and suggests the early

[1] See the fourth article of this series.

[2] The change in temperature will generally increase with the time. The bearing of this fact upon the accuracy of the protracted methods, sometimes counted superior, is clear (see footnote, p. 546).

[3] *E. g.*, by Louguinine and Schukarew, *loc. cit.*, pp. 60, 61.

[4] Louguinine and Schukarew, *loc. cit.*, p. 46.

method, celebrated by Charles Lamb, of roasting pigs by burning down the house. A jacket large enough to steady a rather copious evaporation is easier to control than a room. The evaporation, however, can and generally should be reduced to a small value. An air space of two or three liters inside the jacket is then sufficient and this is open to no objection.[1] If the heat produced by stirring is also kept constant, the three effects included in the usual cooling correction are all very regular.[2]

4. Variations in Procedure.

1. *Choice between the new and the Regnault-Pfaundler methods.*—With a complete jacket the calorimeter temperatures used for the determination of the cooling correction can most simply be referred directly to those of the jacket, if a differential (electrical) method of reading is convenient, or else a correction for the slight variation of the jacket is easily applied. In either case the use of the Regnault-Pfaundler method is not at all interfered with, but the chief reason for using that method is removed and the more direct method of section 1 can often be substituted. The most important difference in the two methods is in the matter of time. With the classical method a correction can usually be applied for changes in the calorimeter constants, while the newer method becomes practically equivalent to the older if extra observations are made so as to determine the value of w (p. 546). Such observations, however, will be needed only occasionally; ordinarily the new method saves nearly ten minutes, or over a third of the whole time demanded by the cooling correction for both observations and computation. This would mean several days in an ordinary series of from 50 to 100 determinations. The new method is at its best when the older method is at its worst, *i. e.*, when the bodies are dropped into the calorimeter, for the rapid temperature rise favors the adjustment of T and φ described on p. 547. Whenever the calorimeter starts at a temperature much below that of the jacket, or the temperature rise is relatively slow, as often in electrical calibration, the older method will often be preferable.

2. *Methods of Computation.*—In Pfaundler's formula, as usually

[1] See p. 581.

[2] See p. 576.

given, a specific method is indicated for obtaining the $\int \vartheta dt$ of formula (9), namely, to add the readings made at equal intervals through the transfer period. If the temperature rise is rapid at first, readings should be taken more often at first than it is desirable to make them later on. In that case, the general method used in this laboratory has some advantages. Readings are made for the first few minutes at the rate of four to the minute. These are added separately and divided by four, and this sum is then added with the other readings, which are taken at one minute intervals. If the observations are first recorded in columns the necessary additions may, without any copying, be performed during the spare time in the last cooling period. The end of the observing thus finds the computation of the cooling correction also practically done, *less than a minute more being required* if the newer method is used.

This method of adding is probably superior in quickness, and certainly in ease, to any graphical method of comparable accuracy. In fact, the only place where graphical methods seem appropriate is in connection with electrical temperature measurement where a null method is used, and where it is therefore necessary to observe the irregular intervals required for equal changes in temperature. There is reason for thinking that even on the score of convenience in reading, this method is inferior to that in which readings are made at regular intervals, a method easily secured by a little attention to the sensitiveness of the galvanometer. That, however, is a question whose consideration belongs elsewhere; as far as the computing is concerned, regular intervals and arithmetical methods seem preferable.

5. VARIATIONS IN THE TEMPERATURE MEASUREMENT.

If the temperature is measured with a resistance thermometer, a change in the temperature of the auxiliary coils will usually cause a change, that is, an error, in the temperature reading, and similar effects may arise from other causes. These changes are ordinarily gradual and small, and hence their rate may be taken as uniform. Their effect on the final result is then the same as that of the factor w, that is, it is a steady variation in the temperature reading, which is independent of the calorimeter temperature. It therefore enters as part of the w correction.

6. Method for Large Temperature Intervals, where K is Variable.

If a given quantity of heat is to be measured, the resulting temperature change can of course be made larger or smaller according to the mass of water heated in the calorimeter. Each procedure has its advantages (see p. 580), but if much of the total error comes in the temperature measurement, as it usually does, an increase in the interval, often to 10°, is altogether preferable. The principal argument against so large an interval is that for it Newton's law of cooling no longer holds. But Newton's law of cooling is no more exact than the similar laws which hold for larger intervals; its only advantage is in simplifying calculation, and this is of little importance in comparison with an increase in accuracy. Moreover, the extra labor needed in computing for larger intervals may be made surprisingly small, and often disappears altogether, even for intervals of 20°.

This ease of computation arises from the fact that for all probable experimental conditions, and with all needful accuracy, the cooling is dependent solely on φ, the temperature difference between calorimeter and jacket.[1]

That is, if V' is the true cooling rate (equal to V, the observed rate, minus w, the small effect due to evaporation and stirring) then

$$V' = f\ (\varphi), \tag{10}$$

which may be put,

$$V' = K\ \varphi',$$

where φ' is another function of φ. But if Newton's law held, we should have had $V' = K\ \varphi$. Hence if for the observed values of φ corresponding values of φ' are substituted, the resulting quantities bear to each other the same relation as obtains where Newton's law holds, and can therefore be treated by any formula based on that law. In other words, since V' is not proportional to φ, we make φ proportional to V' and proceed as before. The labor required is: (1) $f\ (\varphi)$ is observed directly, which requires single observations of cooling, and can be done for a wide temperature range, in duplicate,

[1]Theory of Heat, Preston, 2d ed., 1904, p. 539.

in a day; and (2) values of $\varphi' - \varphi$ are plotted or tabulated against φ. So much is done once for all. Then (3) in each determination the corrections (seldom over eight in number[1]) are looked up for each value of φ and their sum added to the value of Φ. This takes from one to three minutes, which is the maximum increase in time ever demanded by this method of using larger temperature intervals.[2]

To find the error which may result, it will be convenient to begin with the error due to neglecting altogether the variation from Newton's law. It will also be convenient to take first an artificially simple case in which the temperature rises at a uniform rate throughout the transfer period, and the values of the cooling rate, V_0 and V_2, are determined for the end temperatures, t_1 and t_2. (See Fig. 2, where cooling rate, and not temperature, is plotted against time.) Then the cooling correction, computed by any accurate method which assumes Newton's law, will be simply

$$\frac{V_0 + V_2}{2} T_1$$

represented by the area *OPQRN*. But if the true values of V' at the intermediate temperatures lie along the curve XYZ, the true correction is represented by *OPXYZRN*. The error is the difference of these two, represented by the narrow area.

Let V' be given by:

$$V' = A\varphi + B\varphi^2 + C\varphi^3 + + + , \qquad (11)$$

of which it will be sufficient here to consider the first three terms. Now, in this special case, since the temperature rise is linear,

$$\varphi = \varphi_0 + \alpha t$$

Hence, V' can be expressed as a function of constants and t, and the $\int V'dt$ can easily be found. It will be

$$\int_{t_0}^{t_2} \{A(\varphi_0 + \alpha t) + B(\varphi_0 + \alpha t)^2 + C(\varphi_0 + \alpha t)^3\} dt. \qquad (12)$$

[1]For temperatures within a degree of each other, the correction to the average does not differ appreciably from the average correction. Hence a few corrections can be made to answer for a much larger number of observed temperatures.

[2]See, further, footnote, p. 556.

The simply computed correction,

$$\frac{V_0 + V_2}{2} T_1,$$

equals

$$T_1 \left\{ A \frac{\varphi_0 + \varphi_0 + \alpha T_1}{2} + B \frac{\varphi_0 + (\varphi_0 + \alpha T_1)^2}{2} + C \cdots \right\}. \quad (13)$$

On subtracting this from the evaluated integral, and dividing by the temperature rise, $\Delta\vartheta$, the proportional error is obtained, equal to:

$$-\frac{T_1}{6} \Delta\vartheta \left\{ B + 3C \left(\varphi_0 + \frac{\Delta\vartheta}{2} \right) \right\}. \quad (14)$$

In one calorimeter, which holds about 1400 cc. of water, the value of V' up to $\varphi = 20°$ was given by:

$$V' = .00312\varphi + .000083\varphi^2 - .000001\varphi^3 \quad (15)$$

This result can not be assumed to hold for other calorimeters, but it gives a sufficient idea of order of magnitude. In accordance with it and (14) the error in a 10-minute period from improperly assuming Newton's law is only about 1 per mille for a 10-degree interval.

This value, however, is merely an upper limit of the error, which is always less than that just given, for two reasons: (1) The largest contribution to the error comes from the temperatures midway

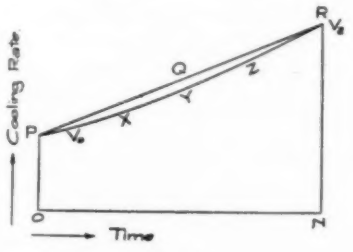

Fig. 2.

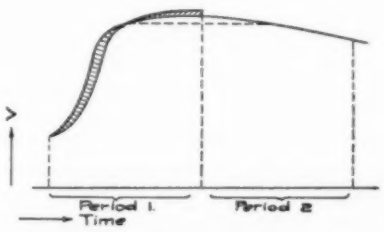

Fig. 3.

between those where the rates are observed. In any actual case these temperatures would prevail for a smaller part of the time. (2) In any actual case, the temperature, after rising, will also fall before the final reading is made. Hence for part of the time there

will be temperatures above the final, as indicated in Fig. 3, whose effect will tend to neutralize that of the lower temperatures. (The error is indicated by the *difference* of the two shaded areas.) As a result, it will nearly always be possible to neglect entirely the variations from Newton's law (for periods of ten minutes or less) for any interval less than 8°, if the accuracy desired is not over .5 per mille, and frequently there will be no error amounting to .1 per mille for any interval up to 20°. The latter has actually been the case in nearly all our own work.[1]

The above formula, (14), supposes two determinations of V as in Pfaundler's formula (9) for the cooling correction. With the simpler formula (5) the expression for the error is more complicated, but its values are not necessarily larger, unless φ_0 is relatively large.[2]

It remains to consider the errors which may arise when the correction is applied. Such an error cannot come from a change in *total magnitude* of the cooling factor, since this is (usually) redetermined for each determination, just as with other methods. The error can only come from the use of a wrong value for the *form* of the curve given in expression(15), that is, a wrong value for the ratio B/A or C/A in that expression. That will of course amount to a wrong value of one or both of the constants B and C. Now, a ten-degree interval is the largest likely to be often needed in practice, and for that the error from neglecting the correction entirely is practically never more than 0.6 per mille; hence not until the variation in B/A had reached the highly improbable value of 16 per cent. would the resulting error be 0.1 per mille.

This conclusion, however, applies only to the case of a consistent error in the correction curve as a whole. It holds because such an error, as shown in Fig.3, is not very effective except in a small

[1]In repetitions of the same determination, or in similar determinations, the chance variations in these small corrections will be negligible in almost any case. The correction found for the first determination can then be applied to other similar ones without any further computation. Hence the three minutes given on p. 554 as the time for computing a large-interval correction is not the time per determination, but rather the time for a whole series.

[2]The full formula in this case is:

$$-T_1\{B(\tfrac{1}{2}\phi_0+\tfrac{1}{6}\Delta\vartheta)+C(\phi_0{}^2+\phi_0\Delta\vartheta+\tfrac{1}{2}\Delta\vartheta^2)\}$$

This corresponds to (14), that is, it gives the upper limit of the error.

part of the whole cooling correction. For accidental irregularities in the values of the different corrections the case is quite different; these corrections evidently must not deviate from a smooth curve by more than the permissible errors in the individual observed values of φ. This requirement is easily met by aid of the following device.

First, let the correction, $\phi - \phi_1$ be denoted by M. Then, according to equations (10) and (11), M equals $V'/A - \phi$, and gives, on addition of ϕ, V'/A as the corrected value of ϕ. But the only requirement for the corrected value of ϕ is that it shall be proportional to V'. It may as well be V'/R, where R is any number; M then equals $V'/R - \phi$ or $(V'/\phi R - 1)\phi$, and there is a range of values of R, easily found by inspection or after a few trials, for which $dM/d\phi$ is in the neighborhood of zero for part of the curve, and small for the rest of it. Precision in the determination of M can thus be easily attained.

7. Procedure with Electrical Thermometers.

The choice of temperature scales is always more or less arbitrary, and the scale furnished by any electrical thermometer is suitable to use directly in determining the cooling correction, even where the method of the preceding section is used. Considerable time is thereby saved, for all preliminary computations are done in microvolts or fractions of an ohm (according to the type of thermometer), and the two final corrected temperatures are the only ones that need be reduced to degrees. This procedure, however, involves an error which is sometimes a little too large to be neglected. It arises as follows: The heat losses during the transfer period are inferred from the temperatures of the calorimeter at that time. Thus, for, instance, a temperature of, say, A microvolts in the second minute of the period indicates a temperature loss of B microvolts during that minute; which corresponds to b degrees. But in the computation the B microvolts are (in effect) added to the similar values for the other minutes, and the sum then added to the observed final temperature, C, to get the corrected final temperature, D, and this corrected temperature is translated from microvolts into degrees. B is therefore really reduced to degrees at the temperature $\frac{1}{2}(C+D)$ microvolts, which is much higher than A, for which B was actually derived, and at this higher temperature B corresponds no longer to b, but to b', degrees. Hence the error. It is proportional to the value of B, to the interval between the temperature at which the cooling, B microvolts, actually occurred, and that for which it is evaluated (that is, to the interval, $\frac{1}{2}(C+D) - A$) and to the rate at which the ratio, microvolts ÷ degrees, changes with temperature. This rate can be taken as constant for copper-constantan thermoelements over intervals of 20°, hence the computation of the error is not laborious. For a fifteen-degree interval the error is only about .1 per mille, unless the calorimeter is already cooling rapidly at the beginning of the transfer period. It is therefore quite negligible in most cases. For the resistance thermometer it is considerably smaller than with the thermoelement.

8. Reduction of the Thermometric Interval.

Although the use of large temperature intervals diminishes the effect of thermometric errors, and is therefore generally to be pre-

ferred, yet there are often occasions where a small interval is desirable or necessary. In such cases, of course, greater thermometric accuracy is needed. This does not necessarily involve any higher proportional accuracy in the temperature interval measured, but rather the extension of ordinary *proportional* accuracy to an extraordinarily small interval, as, for instance, the measurement of a one degree interval to .01 per cent., that is, to .0001°. For this increase in *absolute* accuracy, the mercury thermometer is inadequate. The resistance thermometer and the thermoelement have sufficient precision. The auxiliary electrical measurements with these, however, are somewhat exacting. At ordinary temperatures, .0001° corresponds to a change of only one three-millionth in the resistance of a platinum resistance thermometer; an oil-filled thermostat, surrounding the auxiliary resistance coils, is probably the easiest and simplest means of avoiding the chief resulting difficulties. With the thermoelement a corresponding temperature measurement requires a precision only one tenth as great in the electrical measurements,[1] and the thermostat is usually not necessary, but the precision required is still many times that attained in measuring the temperature interval.

This disadvantage can be almost entirely obviated as follows: The thermoelement is essentially a differential instrument; hence in reading single temperatures with it a comparison temperature is always necessary. For this the ice-bath is commonly chosen on account of its constancy, but it is so far below the ordinary room in temperature that its use commonly necessitates the measurement of intervals considerably greater than those actually employed in the calorimeter. If the comparison temperature is near that of the calorimeter, the temperature differences diminish accordingly, and most of the instrumental errors diminish with them; the maximum precision required anywhere is then comparable with that of the calorimetric observation itself—one ten-thousandth, or less. Such a comparison temperature can be obtained by a suitable comparison body, jacketed like a calorimeter. The temperature of such a body, in general, will not be strictly constant, but the small correction required on account of its variations is a cooling correc-

[1]See The Thermoelement as a Precision Thermometer, PHYS. REV., 31, 154, 1910.

tion, smaller and more certain than the cooling correction for the main calorimeter, and hence it introduces practically no error and almost no inconvenience. For the body can easily be given a cooling factor, K_B, as small as .002. In a 30-minute interval the body will then change only .06 of the mean temperature difference between it and its jacket. Hence for an accuracy of .0001° this difference need be known only to .001°—which is an accuracy far less than that attainable with ease by a differential thermoelement under the given conditions. Again, the jacket will ordinarily have a cooling factor well under .002. A difference of 5° between it and the room for 30 minutes would then cause a change of only 0.3° in its temperature. And with a jacket as constant as this, it is easy to show that a solid block of copper weighing, say, 8 kg., could be used for the comparison body without any error from internal irregularity of temperature. In that case all trouble from evaporation, etc., would disappear, and K_B would always be the same.[1] The comparison body thus requires almost no attention, the calculation required for correcting for its temperature change becomes very simple and easy, while the necessary observations are few, two in a ten-minute interval at most.[2]

The comparison body thus causes less trouble than it saves. Its possibilities in the direction of accuracy are evident. Furthermore, the correction which it introduces is simple, usually familiar, and easily controlled by simple tests, while the errors which are avoided depend upon the quality or constancy of electrical apparatus, etc., and are especially hard to detect. The comparison body, therefore, particularly increases the certainty and ease of the measurements, and therein, perhaps, lies its greatest value.

The only uncertainty worthy of mention concerning the comparison body just described relates to the magnitude of the effect which the room temperature may produce through conduction along the thermoelement. There is no question that such effect can be abso-

[1]An uncertainty of several per cent. in K_B, however, would ordinarily be permissible. The use of such a block, though perhaps the best and simplest way, is, of course, not the only satisfactory way of obtaining a comparison temperature.

[2]The jacket, with its stirrer, is easily made into a thermostat, in which case no correction at all is needed, but, in view of the ease with which the correction can be made, it is perhaps more advantageous to apply it.

lutely prevented, if necessary—for instance, by leading the thermo-element in through the water of the jacket. If such an effect is present, however, it will probably affect the calorimeter also, in which case the effect on the body will tend to act as a compensation, and may be a positive advantage.

SUMMARY.

1. The oft-noted uncertainties in the calorimetric cooling correction are usually due to changes in room temperature and to evaporation. For the greatest accuracy, and usually for convenience also, it is well to have: (1) A jacket whose temperature is measured directly, completely surrounding the calorimeter; (2) the calorimeter cover in contact with the water so that all bodies at uncertain temperatures are avoided; and (3) evaporation made very small. The difficulties of the cooling correction then largely disappear.

2. This system facilitates a method of computing the cooling correction which requires but one cooling period, and but one minute's arithmetical work after observations are finished. The method is especially advantageous where bodies are dropped into the calorimeter.

3. Ordinarily, in accurate calorimetry, a very small temperature interval is used, in order that the observer may have the advantage of assuming Newton's Law of cooling in his computations. This magnifies the effect of thermometric errors. To make a correction for the variation from Newton's Law not only increases accuracy in most cases, but does not increase appreciably the labor of computation. The procedure is this: Since the cooling rates are not proportional to the temperatures, the temperatures are simply corrected so as to be proportional to the rates; all the ordinary formulæ can then be applied. For ordinary accuracies, the correction can be disregarded up to 8°. With the correction, deviations from Newton's Law cause no error in 20° intervals.

4. If a small interval is necessary, the preceding method can not be applied. The required absolute accuracy in temperature measurement can then usually be obtained by electrical methods, but with these, as usually conducted, the electrical quantity measured

corresponds to a relatively large temperature interval (20° to 300°), so that great precision is required. This difficulty is avoided if, with the thermoelement, the customary ice bath is replaced by a comparison body in a water jacket. The correction for its change is only a cooling correction, and does not materially affect the total error, since the regular calorimeter necessarily has a larger and more uncertain correction of the same kind, or something equivalent. The net gain is a considerable simplification of the problem of accurate temperature measurement, where intervals and not absolute temperatures are required.

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WASHINGTON, D. C., July 15, 1910.

LAG EFFECTS AND OTHER ERRORS IN CALORIMETRY.

BY WALTER P. WHITE.

I. LAGS.

JAEGER and von Steinwehr[1] have shown how errors may arise in calorimetry from the time lag of the thermometer. Later, but independently, T. W. Richards[2] noted the same possibility, and also the possibility of an error from lag in the air currents which cause the cooling itself. Still other lag effects have since been pointed out.[3] The thermometric lag effect is here shown to be much less important than was at first supposed by the above writers.

The general character of all the lags can perhaps be most conveniently presented by proceeding at once to the most familiar case, that of thermometer lag.

1. *Thermometric Lag.*

(*a*) Mathematically, it will be sufficient to consider the very simple and familiar system of two bodies only, one of which receives heat from the other, and at a rate proportional to their temperature difference. If the change in the primary body occurs at a uniform rate, so that its temperature during any such change may be expressed as $A + Vt$, the temperature of the secondary varies according to the equation:

$$-\frac{d\vartheta}{dt} = K(\vartheta - A - Vt). \qquad (1)$$

Solving this:

$$\vartheta = A + Vt - \frac{V}{K} + \left(\vartheta_0 - A + \frac{V}{K}\right)e^{-Kt}. \qquad (2)$$

[1] W. Jaeger and H. von Steinwehr, Verhandl. der Deutsch. Physik. Gesellschaft, 5, 50 and 353, 1903; Zeitschr. f. Phys. Chem., 54, 428, 1906.

[2] T. W. Richards, L. J. Henderson, and G. S. Forbes, Proc. Amer. Acad., 41, 4, 1905; Zeitschr. f. Phys. Chem., 52, 551, 1905.

[3] PHYS. REV., 27, 526, 1908; 28, 464, 1909.

After a steady condition is reached, this becomes:

$$\vartheta = A + Vt - \frac{V}{K}, \tag{3}$$

so that $1/K$ is the time lag, V/K, the temperature lag of the secondary behind the primary when the rate of primary temperature change is constant. For constant primary temperature:

$$\vartheta = (\vartheta_0 - A)e^{-Kt} + A. \tag{4}$$

If the primary is itself cooling (with constant cooling factor k) toward a third body of fixed temperature, B, its temperature is given by (4), and instead of (1) we have, for the secondary:

$$-\frac{d\vartheta}{dt} = K[\vartheta - (A - B)e^{-kt} - B], \tag{5}$$

whence

$$\vartheta = B + \frac{K}{K-k}(A-B)e^{-kt} + \left\{\vartheta_0 - B - \frac{K}{K-k}(A-B)\right\}e^{-Kt}. \tag{6}$$

If the temperatures are measured from B (*i. e.*, $B = 0$), (6), by a little rearranging, takes the form:

$$\vartheta = \left(1 + \frac{k}{K-k}\right)Ae^{-kt} + \left\{\vartheta_0 - A - \frac{k}{K-k}A\right\}e^{-Kt}, \tag{6a}$$

which will be used presently. If the lag of the secondary is much smaller than that of the primary, the third term will vanish before the second, and then the temperature difference of the two bodies will be:

$$\frac{k}{K-k}(\text{primary temp.} - B) = \text{say, } l, \tag{7}$$

which is the temperature lag between two bodies cooling steadily in this way.[1]

[1]The time lag is then the time required for the secondary temperature (ϑ) to reach any value of the primary, $[(A - B)e^{-kt} + B]$. That is, if τ is the time lag:

$$(A - B)e^{-kt} + B = B + \frac{K}{K-k}(A - B)e^{-k(t+\tau)}, \tag{8}$$

whence

$$1 = \frac{K}{K-k}e^{-k\tau}$$

or

$$e^{k\tau} = \frac{K-k}{k}. \tag{8a}$$

This gives, very closely if k/K is small,

$$\tau = \frac{1}{K}\left(1 + \frac{k}{2K}\right). \tag{8b}$$

(*b*) Jaeger and von Steinwehr's formula for the lag effect may be derived as follows: Let the calorimeter be originally at the temperature of the jacket (which is also taken as zero); let it be heated to a temperature ϑ_y degrees higher, then allowed to cool spontaneously, and so made to traverse the temperature time curve *DE* (Fig. 1) as far as $\Delta\vartheta$. At *D* there is no lag, since *V* (the cooling rate) is zero. At *E*, $V = k\Delta\vartheta$, if *k* is the cooling constant of the calorimeter itself, hence, taking the thermometer as the secondary body, its temperature lag is then

$$l = \Delta\vartheta \frac{k}{K} . \qquad (9)$$

If the initial temperature is not that of the jacket, there will be a lag effect at the beginning also, but the difference of the two lag effects, and therefore the error, will be the same. This is so nearly obvious that it has seemed well to simplify the presentation, here

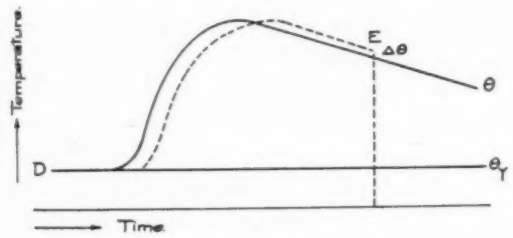

Fig. 1.

Temperature-time curves of calorimeter and thermometer, simplified, with lag exaggerated.

and later, by arbitrarily assuming an initial temperature equal to the jacket. *k* is usually about .003° per minute per degree difference of temperature. In a mercury thermometer of 10 seconds lag, *K* is 6 (the time unit being the minute), hence the error for it would be .0005, or 0.5 per mille.

(*c*) The effect of lag during the temperature rise appears at first sight negligible, since the temperatures measured at this time are used only for computing the cooling correction, and hence need only about one twentieth the accuracy required for the final value.[1] But a countervailing circumstance is found in the fact that the

[1]See p. 550.

rate of temperature change is more rapid during most of the time while the temperature is rising. In fact, if this time is T, the average rate of rise will be $\Delta\vartheta/T$, and the average thermometer *temperature* lag, l, will be $\Delta\vartheta/KT$. The resulting effect on the cooling correction will be this lag multiplied by the cooling factor and the time, or

$$\frac{\Delta\vartheta}{KT} \times kT = \frac{k}{K}\Delta\vartheta,$$

which is numerically equal to (9). The effect of thermometer lag on the cooling correction, therefore, will just about offset the effect on the end temperature, and the error from thermometric lag will be nearly negligible. Of course, this assumes that all the readings are made with the same thermometer or with thermometers having the same time lag. If an electrical thermometer of negligible lag is used for the end temperatures, and a mercurial for the rapid rise, the lag error will be that due to the mercurial thermometer, and will be larger than if that had been used exclusively.

(*d*) A more comprehensive demonstration is the following: Suppose a thermometer of time lag τ is used to read the curve of Fig. 1. Suppose a lagless thermometer is also available, and that it is read

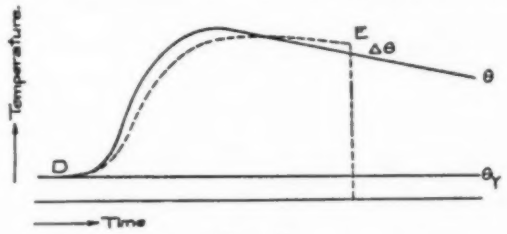

Fig. 2

Temperature-time curves of calorimeter and thermometer. The lag is exaggerated.

every time the other is, but τ seconds earlier each time. The readings of the two will be identical (to an order of precision which will be investigated presently). But those of the lagless thermometer must give a final result unaffected by lag. Hence the others must also. The same applies if the curves are extended through the cooling periods, hence the lag effect during those periods does not introduce any error.[1]

[1] A comparison of the two demonstrations shows the advantage that often may come from treating lags as primarily a question of time rather than of temperature.

(*e*) The assumption just made, that the thermometer is always the same number of seconds behind the calorimeter in its reading, is evidently false at the turning points of the primary curve, and the real relation of the two is more nearly shown in Fig. 2, where the dotted curve is for the thermometer. And while the resulting "secondary effects" are not large, it is not evident that they are negligible, especially if the temperature rise is rapid. A more rigorous treatment of the lag effect will therefore now be given. (The conclusions are stated on p. 567.)

Suppose, first, for simplicity, that the temperature curve of the primary body—that is, of the calorimeter—is composed of successive short straight portions, which may be as numerous as we please. Suppose also that after rising in this way, the temperature falls toward that of the jacket in accordance with (4), as usual. For any short portion, the nth, let the time be T_n, the (constant) rate V_n, the temperature rise, therefore, $(VT)_n$. The initial temperature (as well as the temperature zero) may be taken as that of the jacket; the temperature at the beginning of each interval is that at the end of the previous one; the time may be measured from a new zero for each interval. The quantity to be found for each interval and for the whole time is the integral of the temperature lag, l. Let L_n be the value of l at the end of any interval. During the short intervals $l = A + Vt - \vartheta$. Inserting this variable, equation (2) becomes, for the nth interval,

$$l_n = \frac{V_n}{K}(1 - e^{-Kt}) + L_{n-1}e^{-Kt}, \tag{10}$$

whose integral for the interval is;

$$\int_0^{T_n} l\,dt = \frac{V_n T_n}{K} + \frac{1}{K}\left(L_{n-1} - \frac{V_n}{K}\right)(1 - e^{-KT_n}). \tag{11}$$

Rearranged, this is:

$$\frac{V_n T_n}{K} + \frac{L_{n-1}}{K} - \frac{1}{K}\left[\frac{V_n}{K}(1 - e^{-KT_n}) + L_{n-1}e^{-KT_n}\right]. \tag{11a}$$

But the bracketed expression is merely a particular value of the second member of (10), and therefore equals L_n, whence the integral is:

$$\int_{T_n} l\,dt = \frac{1}{K}\{(VT)_n + L_{n-1} - L_n\}. \tag{12}$$

The sum of the integrals is at once evident. The L's enter with opposite signs, and will therefore vanish in the summation, all but the first and last, and the first, L_0, is zero by hypothesis. The total integrated lag for all the short intervals is, then, if T_y is the last short interval:

$$\frac{1}{K}\{\Sigma(VT) - L_y\}. \tag{13}$$

The final, or Zth period remains, during which the calorimeter cools regularly, according to the exponential law, that is, according to equation (4). For it, by inserting l, (6*a*) becomes:

$$l_z = \frac{k}{K - k}A_z(e^{-Kt} - e^{-kt}) + L_y e^{-Kt}. \tag{14}$$

T_x is of course great enough to make the exponential e^{-KT_x} vanish, so the integral of l_x becomes:

$$\frac{k}{K-k} A_x \left(\frac{1}{K} - \frac{1}{k} + \frac{e^{-kT_x}}{k} \right) + \frac{L_y}{K}. \tag{15}$$

But $A_x = \Sigma(VT)$ and $A_x e^{-KT_x}$ is the final temperature of the calorimeter, or $\Delta\vartheta$, hence (15) becomes:

$$-\frac{1}{K}[\Sigma(VT) - L_y] + \frac{\Delta\vartheta}{K-k}, \tag{16}$$

which, added to (13), gives for the final value of the integrated lag for the whole time:

$$\frac{1}{K-k}\Delta\vartheta. \tag{17}$$

Multiplied by k, the cooling constant of the calorimeter, this gives

$$-\frac{k}{K-k}\Delta\vartheta$$

as the true error in the cooling correction due to thermometric lag. But

$$+\frac{k}{K-k}\Delta\vartheta$$

is, by (7), also the true error in the final temperature due to lag. Hence the error from thermometric lag is rigorously zero for the conditions assumed.[1]

This result is independent of the choice of the individual short temperature differences. Hence these may be made to approach as close as we please to any curve whatever, no matter how broken it may be. The result just obtained, therefore, is perfectly general.

The final expression contains no term depending on the form of the primary temperature curve. Hence the rapidity or slowness of heating (for instance) has no effect whatever on the amount of error from thermometer lag, except in so far as very slight variations may arise because the actual experimental conditions are not quite so simple as those assumed for the mathematical treatment. These minute variations are the only "second order effects" tending to cause any error from thermometer lag.

[1]If the temperature rise ends at the jacket temperature, A_x is zero, and (15) reduces to $+ L_y/K$. But in that case, L_0, omitted from (13), is, by (7),

$$\frac{k}{K-k}\Sigma VT = \frac{k}{K-k}\Delta\vartheta.$$

(13) thus becomes:

$$\frac{1}{K}\left(\frac{K}{K-k}\Delta\vartheta - L_y\right),$$

and (17) is as before. The same can easily be shown to be true for any other initial temperature. The simplification obtained by starting at the jacket temperature has therefore had no effect on the result.

2. *General Characters of Lag Effects.*

The effects of the other lags as here treated concern the cooling correction, or the final temperature, alone, and hence do not finally vanish like that of the thermometer lag. But all tend to have the essential characteristics of the thermometric lag effects as far as that applies to the cooling correction. That is, (1) they are proportional to the total temperature rise, for the same apparatus and procedure; and (2) they are largely independent of the rate of heating.

They are most conveniently stated in terms of time. Thus in Fig. 1 or 2, the cooling correction is approximately represented by the product of the cooling factor, k, and the area $ABDE$, and this area represents the product of temperature difference (of calorimeter and jacket) and time. If the readings from which the cooling is computed (dotted curve) are consistently later (or earlier) than the cooling itself by a time, τ, the whole area will be in error by an amount (areas to the left of the dotted line) equal to $\tau\Delta\vartheta$, and the cooling correction itself will be in error by $k\tau\Delta\vartheta$.[1] Since $\Delta\vartheta$ is very nearly the final temperature, the proportional error is approximately $k\tau$. For instance, .003 per minute is about the cooling factor of a one-liter calorimeter. With it, a time lag of 1 minute, affecting the cooling correction, will produce an error of .003; a 20-second lag causes an error of .001, while to obtain an accuracy of .0001 (0.1 per mille) requires a precision of 2 seconds in the average timing of the observations.

3. *Internal Lag.*

For simplicity, the initial temperature will be assumed equal to that of the jacket, as already explained, page 564.

When a calorimeter is cooling, there will be present in it temperature differences which even vigorous stirring will not wholly prevent. Three different errors may result: (1) During cooling the surface, on which the cooling really depends, will be at a lower temperature than the thermometer, whose reading is used in calculating the cooling rate. And since in that calculation the (too high) thermometer reading comes in the divisor, the cooling factor (K) ob-

[1] This is, of course, the same as (9).

tained will be too low. (2) The final mean temperature will also tend to be read too high. (3) The high thermometer reading during heat transfer to the calorimeter will tend to make the cooling correction come too high.

All these effects will occur in addition to and independently of the thermometer lag itself.[1] They will vary with the position of the thermometer, which usually may be so placed as to make any one become zero or even change sign. (In fact, it will often be easy to locate the thermometer at a place where the temperature is equal to the mean final temperature, or, in some calorimeters, where the temperature during heating is equal to the average over the surface. But the final surface temperature is less likely to be given by the thermometer.)

The magnitude of each error is easily stated. If l_1 is the lead during heating,[2] the resulting error in the final corrected result is, by (9), $+ l_1 k\Delta\vartheta$. The error due to lag in the *mean* final temperature has the same form, $l_m k\Delta\vartheta$, being equal to the lag times the cooling rate, but it is usually much smaller, since l_m is usually less than l_1. Similarly, the error in the final *surface* temperature is $+ l_3 k\Delta\vartheta$, so that this temperature as observed becomes $\Delta\vartheta(1 + l_3 k)$. The resulting error in the cooling factor,

$$\left(\frac{V_3}{\Delta\vartheta_3} = \frac{k\Delta\vartheta \text{ (real)}}{\Delta\vartheta \text{ (observed)}}\right) \text{ is } l_3 k^2$$

and the error in the cooling correction is $- T_1\Delta\vartheta l_3 k^2$, which is the final error from this cause. Since it contains the square of the small quantity, k, it is evidently negligible, unless T_1 or l_3 is very large indeed.

The order of magnitude of each of these errors is easily found by thermoelectric measurements. The investigation of the final temperature distribution calls for a sensitive element of many junctions. Since the readings may be differential, with the element totally immersed, no attention need be paid to the homogeneity of the wire.[3]

[1] And hence, in measuring them, the thermometer lag must not be included. If a lagging thermometer should have the same temperature as the surface, this would not indicate the absence of error from internal lag.

[2] For the significance of the subscripts and the rest of the notation, see pages 545–6.

[3] Such an element, with 10 couples, easily sensitive to .0002°, was made and inclosed complete in two and one-half hours.

The temperature lags in which the surface is involved concern the cooling correction, and hence need less accuracy in the temperature measurement. A single thermocouple is sufficient, whose outer junction is perhaps best soldered directly to the calorimeter wall. The lag during heating can be measured as the calorimeter passes through the jacket temperature; all parts of the thermocouple will then be near the same temperature, and there need be no fear of error from inhomogeneity. During cooling the temperature lag is necessarily very small compared to the temperature difference between the calorimeter and the air, hence for this test, unless the thermocouple is unusually homogeneous, it should run through the water, where the temperature is nearly uniform. This can be done successfully if the wire is insulated and well paraffined, but it requires care; hence it is fortunate that this particular lag is not important.

All these lags depend greatly on the design of the calorimeter as well as on the position of the thermometer, hence isolated data in regard to them will have little general application. But it is certainly easy to bring the internal final temperature difference below $.0003\Delta\vartheta$, and the lag of the surface during heating below 3 seconds—though not without producing a perceptible temperature rise by stirring. (In the case investigated, .001° per minute.) The greatest error from these lags would be, in absolute measurements, less than .0002, and in a calibrated calorimeter, of course, practically nothing.

4. *Outlying Portions of the Calorimeter.*

The use of felt packing to diminish direct heat loss from calorimeters has long since been abandoned on account of the great complication and uncertainty thereby introduced into the cooling correction. For the same reason, all outlying parts of the calorimeter may advantageously be reduced in size or dispensed with altogether if possible. The irregularities introduced by unavoidable projections can then be satisfactorily corrected for. They depend mainly on three things: (1) The mean final temperature of the projections, which will be a little different from that of the water in the calorimeter. (2) The time required to reach this temperature —no change in the thermal condition of the projections involving

an appreciable quantity of heat should occur after the end of the transfer period. (3) The lag in the total cooling itself, due to the initially lower temperature of the projecting surfaces.

The nature and magnitude of these effects in the case of such bodies as thermometers are under investigation in another quarter, and hence need not be dwelt on here. For metal parts, all three are generally small, as can easily be shown by thermoelectric measurements. For instance, in the calorimeter just mentioned, the projecting portions at the top, which were 2 cm. high, lagged 10 seconds behind the water. Effect (2), therefore, is for them far more than negligible. They formed less than a tenth of the surface, hence for them effect (3) was equivalent to a lag of less than 1 second for the whole cooling correction. Effect (1) is not determined by the above measurement, but is very small; moreover, both it and (3) are proportional to the temperature rise, and hence eliminated if the calorimeter is calibrated. All the errors, therefore, from imperfect temperature equalization in the *metal* projections of a well designed calorimeter are quite negligible, except in absolute determinations of the utmost precision, and hardly appreciable even then.

5. *Lag of the Air Currents.*

The thermal effects of the air are more complicated than those of the metallic projections, for its final mean temperature differs appreciably from that of the calorimeter, and the flow of heat into it is dependent on convection currents which start only after some heat has already passed from the calorimeter. Hence it seems preferable to treat the air as purely environing material, ignoring its heat capacity. There are then two disturbing effects, a "lead" of the cooling, due to the air's being colder at first, and a lag, due to the time required to start the convection currents. The (approximate) time required for both these to disappear was investigated experimentally as follows: Two square tin cans were placed near each other, with their adjacent faces parallel and 3 cm. apart. One was filled with cold water to imitate the effect of the jacket; the other contained warmer water and represented the calorimeter. The intervening air space was shielded against drafts. The air lag may possibly be greater if the convection currents have to be started

from a condition of rest, and it seemed preferable to examine this case. Hence the determinations were made by quickly pouring the warm water into its can, previously brought to room temperature. The rise of temperature thus produced was about 5°. A fine thermoelement (whose own lag needs consideration) gave the temperature of the air. It was read every 2 seconds after the pouring until steady. Results agreed to 1 second. In some cases, the discrepancy was evidently due, wholly or in part, to variation in the time of pouring.

The lag of the thermoelement was determined by swinging it suddenly over to within about 3 mm. of the (then) already warm can. The first part of the resulting curve, treated as exponential, that is, by equation (4), indicated a lag constant of about 4 seconds for the thermoelement (and galvanometer). The curve obtained on pouring water in, with the element fixed at the same distance, contained the effect of both lags, and treated as such, by equation (6) (with some approximations) indicated about 4 seconds for the air lag constant alone. Now the heat lost by the surface in regularly cooling would raise a layer of air 1 cm. thick to its own temperature in 3.5 seconds, hence in this case the surface lost less than the normal amount of heat in the first few seconds, the difference amounting, all things considered, to a lag of some 2 ± 1 seconds. Another trial of air lag was made at a point 2 cm. away from the warmer can. The air lag constant here was nearer 9 seconds. But the time required to heat the whole air layer at the normal rate of loss from the calorimeter was 6 ± 1 seconds.[1] Hence this result agrees with the other within the observational errors, and therefore, since most of the systematic errors affect the two differently, confirms it very well. A comparison of the two shows that the normal heat flow is established very quickly at the surface of the calorimeter, and that the air lag there is not appreciably increased by having a rather large space between calorimeter and jacket. This is important, since to avoid errors from evaporation it is often desirable to have this space rather large (see p. 551).

These results, in spite of their large proportional error, seem

[1] That is, 5 seconds if the air were all heated before any heat escaped to the colder surface—hence a little more in practice.

sufficient for their purpose, since they show that the total lag is almost negligible, and since a more exact result at one point would give no better idea of the mean effect all over the calorimeter. With slow instead of sudden heating, the lag would be less if it differed at all. The air lag effect, then, is about 0.1 per mille for a one-liter calorimeter (see p. 568), and might cause a slight uncertainty in an absolute determination of the highest precision. In a calibrated calorimeter it is quite negligible, since only its variations are a cause of error.

On the whole, then, if exception is made of non-metallic projections from the calorimeter, not here considered, no lag effect need cause any error even approaching 0.1 per mille in a calibrated calorimeter of ordinary size, and in absolute determinations the maximum probable systematic error from all lags does not exceed 0.2 per mille, a quantity considerably smaller than the disagreements among the most accurate calorimetric determinations yet reported. But this conclusion, of course, presupposes the strict "two-temperature system" of jacket and calorimeter proposed in the preceding paper — that is, the absence in the calorimeter chamber of large blocks of ebonite or cork, of covers not touching the water, or of any considerable masses or surfaces not at the temperature of the water in either calorimeter or jacket.

II. Other Calorimetric Errors.

Beside lags, the following seem the most important sources of error: (1) The cooling correction, which, as ordinarily treated, covers: (*a*) evaporation, (*b*) the heat produced by stirring, (*c*) the true cooling, or direct heat loss; (2) time measurement; (3) temperature measurement.

1. (*a*) *Evaporation.*

A calorimetric determination seldom involves a quantity of heat greater than 6,000 calories. The evaporation of 10 mg. of water consumes 6 calories. Hence an irregularity in evaporation amounting to 10 mg. limits the accuracy to 1 per mille, and all the water in or on the calorimeter must be accounted for to a milligram to reach the accuracy, 0.1 per mille, which is often attainable in the temperature measurements and in the effect of the true cooling correction.

For a recent combustion calorimeter, intended for work of the highest precision, the evaporation was about 10 mg. per minute.[1] This involved a heat loss as great, on the average, as that from the true cooling itself, and far more uncertain. An irregular variation in it of 1 per cent. in 10 minutes would be fatal to the highest accuracy. The direct exposure of such a calorimeter to the air of even a carefully regulated room seems at best an awkward way of securing high accuracy. Control of the evaporation seems simpler, even aside from any question as to the use of a complete jacket. The control of the evaporation also removes the only important objection to the complete jacket (cf. page 550).

The essential point in controlling evaporation is evidently that the evaporation must be dependent only on the jacket and calorimeter temperatures — it must not vary with time, for instance. Two general methods meet this requirement. (1) If the calorimeter itself is open and the jacket closed, the intervening space may become saturated, and the evaporation becomes a distillation, which may continue fairly regularly for a long time. If the calorimeter is cooler than the jacket the rate of distillation becomes zero, and there is less chance of irregularity. In either case, if time is first allowed for the space to become saturated, if the space is not afterward opened, if it is small, and if the temperature rise in the calorimeter is not over 2 or 3 degrees, then it is easy to show that the increase of water vapor in the space resulting from the temperature rise will not cause appreciable error. In some cases, of course, all these conditions may not be necessary.[2] (2) In general, it seems surer, and in some ways simpler, to check the evaporation at the calorimeter by a fairly tight cover. Such a cover should preferably be in contact with the calorimeter water, as otherwise the cover will constitute a third body in the system, one whose temperature is different from either jacket or calorimeter. A very simple form of cover in contact with the water is the light floating cup first used in this laboratory (1907). The ordinary rate of evaporation (30 mg. per hour at 24°) with such a cup, however, is undesirably large, and is unnecessary. A fairly tight cover is preferable, and can easily

[1] Jaeger and von Steinwehr, Ann. d. Phys., *21*, 52, 1906.

[2] For the partial study of such a case, see T. W. Richards and L. L. Burgess, Jour. Amer. Chem. Soc., *32*, 449, 1910.

be made quite satisfactory. One such will be described in a subsequent article.

The evaporation of small amounts of water from the outside of the calorimeter is especially serious, because the water will frequently be all gone before the end of the cooling period, so that there is no indication of what has occurred. This may result from a minute drop left on the outside after filling, or from condensed or adsorbed moisture. It is therefore necessary to exercise care in filling the calorimeter, and also to avoid every chance of excessive moisture in all work where the calorimeter is cooler than the jacket or exposes any considerable surface of hygroscopic material, or often, perhaps, to avoid the last two conditions altogether. A tarnished copper surface 100 cm. square adsorbed 7 mg. of water in a saturated atmosphere at ordinary temperature. A surface of polished nickel of the same size under the same conditions adsorbed indefinitely less than 0.1 mg.

1. (*b*) *The Heat Produced by Stirring.*

The heat of stirring is eliminated in the cooling correction, so that only its variations remain as a source of error, and since the heat is small and the speed of the motor can be regulated if necessary, an appreciable error from this cause can always be avoided. The only question is as to how easily this can be done. Data here are rather meager, but a partial answer can be given.

The object of stirring is to equalize temperature, or, more definitely, to avoid the three lag errors discussed in section 3, page 568. But, as there shown, the surface lag during heating is the most serious, and therefore it may be taken as the measure of the error from insufficient stirring. One calorimeter (calorimeter *A*, which will be more fully described in a subsequent article of this series) was heated about .001° per minute when this lag was 3 seconds, that is, 0.15 per mille of the temperature interval. The smallness of lag is probably roughly proportional to the speed of stirring. The heat was found to vary about as the cube of the speed. The proportional error will of course depend on the temperature rise employed, and on the length of the transfer period. For ten minutes, therefore, for a two-degree rise, and for stirring as just de-

scribed, a variation of 1.5 per cent. in the speed causes a final error of 0.1 per mille. But the heat can be reduced to a tenth or even a hundredth by a reduction in the speed which would not ordinarily make the lag error appreciable. (The lag error, of course, is only the variation in the lag.) It seems probable, therefore, that the necessity for a governor can nearly always be avoided; but that this would generally require, for work of high precision, a suitably designed calorimeter, and some care in determining the proper speed of stirring.

With any calorimeter, the possible disadvantage of an unnecessarily high speed of stirring is clear. Equally clear is the advantage of any feature of calorimeter design which facilitates equalization of temperature, for a moderate gain in this direction may render possible a very considerable reduction in the heat of stirring.[1]

The numerical results just cited agree very well with some recently published by Richards and Burgess,[2] not only as to the variation of heat with speed, but also as to the amount of heat produced when stirring is effective. They used an up-and-down stirrer, while calorimeter *A* has a propeller; whence it would appear that there is little reason for the opinion that a propeller gives more heat for the same efficiency. The prevalence of this opinion is perhaps explained by Richards and Burgess' observation that in most previous calorimetric determinations with reciprocating stirrers the stirring has been insufficient.

1. (*c*) *The True Cooling.*

The irregularity commonly attributed to the cooling correction seems mainly chargeable to evaporation, stirring, and variable environing temperature. With these removed, the available evidence indicates that the cooling is ordinarily quite negligible as a source of error. Cooling corrections seldom reach 3 per cent. of the total temperature rise. For a final accuracy of 0.1 per mille, therefore,

[1]Some calorimeters have the stirrer in a side tube which is much narrower than the main vessel. Since the speed of the water in this narrow tube must be relatively high for any given effectiveness, this arrangement is evidently defective as far as heat production is concerned, though it may sometimes be justified by the necessity for reducing the total mass of water.

[2]*Loc. cit.*, p. 446.

the cooling need be regular only to one three-hundredth. Numerous direct observations have shown that its irregularities are not one third of that, and this limit is merely that set by the temperature measurement.

The cooling of the calorimeter, however, is a source of error indirectly, for the determination of the cooling rates calls for additional accurate thermometric measurements. The increase of error here results simply from the multiplication of observations, and is independent of the accuracy or magnitude of the correction itself. Indeed, it is as great in methods where the cooling is eliminated (adiabatic methods), if observations are still needed to show the magnitude of evaporation or stirring effects.

The determination of the cooling rates is sometimes omitted, and the correction is found directly from a mean rate, which is determined once for all, and assumed to be constant. This method is generally used to save time at the expense of accuracy, but will evidently be an aid to accuracy also if the cooling rate can be made anywhere near as consistent from day to day as it is during a single set-up of the apparatus. With calorimeter *A*, the rate was not thus consistent. An attempt to determine the reasons was interrupted, but gave the following results:

There was no appreciable temperature coefficient of the cooling rate. That is, the rate for a given temperature difference of jacket and calorimeter was not perceptibly changed when both were raised 5°.

There was no perceptible effect from very large changes in the humidity of the air in the calorimeter chamber.

The rate was very sensitive to changes in the condition of the surface of the calorimeter and its chamber, and this may have been the sole cause of the variations.[1]

On the whole, it appears probable that the cooling rate can often be made constant enough to avoid the accidental error resulting from its continual redetermination and certainly enough to allow a considerable saving of time where maximum accuracy is not required. (See further, sec. 3, *g*, pp. 581–582.)

[1] A thin coat of paraffin raised the cooling rate about 15 per cent. The copper cover of the calorimeter had not been nickel-plated at this time, and its slow oxidation and occasional cleaning with acid were clearly perceptible in the cooling rate.

2. *Time Measurement.*

It has been shown (p. 568) that with a calorimeter of one liter capacity, an average error of 2 seconds in the timing of measurements corresponds to an error of about .0001 (0.1 per mille). Measurements (involving the estimation of tenths) can be timed at least to one third of a second. Hence not till an accuracy of .00002 (0.02 per mille) is to be surpassed will there be serious error from this cause.

Where the jacket has to be opened (in order to drop a body into the calorimeter, for instance), the cooling correction will be different for a short time. If, for instance, the cooling rate with jacket open is different by one tenth, the opening might continue for 20 seconds with an error of only 0.1 per mille. Hence this source of error is not serious, except when very hot furnaces are near.

3. *Temperature Measurement.*

Since the other errors can, with no great difficulty, be brought below one part in 30,000, the principal obstacle to accuracy at present lies in temperature measurement. In measuring a continuous variable, like temperature, the error of a single observation, even with perfect judgment on the observer's part, may be half the smallest unit recorded, and will be one fourth of that on the average. But errors in judgment and in the apparatus will also occur. Ordinarily, also, in calorimetry, from 4 to 10 quantities (observations and corrections) will contribute to the final result; and this will, of course, cause a final accidental error several times that of one observation; averaging will diminish the final error, but not greatly unless the averages are carried out to the next decimal place. On the whole, the average final error will lie between 0.5 and 1.5 of the smallest unit recorded. An average error larger than 1.5 would indicate that the precision of the single readings was somewhat fictitious.

It follows: (1) That with mercury thermometers reading to .001° the error in a 20-degree interval would still be mainly due to temperature measurement, and that an increase of the interval to 20° should increase the accuracy if the calibration of the thermometer

were good enough; (2) that even with thermometers accurate to .0001° there is generally a gain in accuracy, as far as the calorimeter itself is concerned, in increasing the interval at least to 5°.

III. Applications and Conclusions.

1. *Conclusions as to All Errors.*

If no source of error has been overlooked, it follows from the preceding that in general the main source of error, not easily preventable, in the calorimetric method of mixtures, is that inherent in the thermometric measurements. On this basis an accuracy of .0001 should not be counted remarkable. Errors in time measurement and all lags may be made negligible save in the most refined absolute measurements. And in particular, contrary to common opinion, the error in the cooling correction should not be appreciable.

Experimental corroboration of the conclusions here reached as to the importance and magnitude of cooling correction and thermometric errors will be given in a subsequent paper of this series.

2. *Choice of Methods.*

The foregoing indicates the most favorable procedure in a number of cases.

(*a*) *Shape.*—The effect of the form of the calorimeter on the cooling correction is slight. The resulting effect on the final accuracy is, in accordance with the preceding section, quite negligible. The effect of the shape on facility of stirring will generally be worth consideration.

(*b*) *Surface.*—The surface of the calorimeter should not be hygroscopic. It is decidedly advantageous if its condition can be made constant (p. 577). There is some doubt, perhaps, whether constancy can best be secured by a highly polished surface whose cleanliness can be assured, or by a surface whose radiating power is rather high, and therefore not likely to be further increased. The resulting difference in the cooling rate, perhaps 20 per cent., is, comparatively, of little importance.

(*c*) *Method of Stirring.*—Louiginine and Schukarew state[1] that the up-and-down methods of stirring cause greater evaporation than

[1] *Loc. cit.*, p. 27.

the propeller methods, but prefer them on account of the smaller heat production. Since the heat of stirring is slight and easily controlled in any case, while evaporation is far more troublesome and since it is doubtful (see p. 576) if the heat production is any smaller with the reciprocating stirrer, the propeller seems preferable wherever the design or arrangement of the calorimeter do not make it inconvenient.

(*d*) *Size of Calorimeter, or Smallness of Temperature Interval.*—For a given quantity of heat the temperature interval is inversely proportional to the size (strictly, to the heat capacity) of the calorimeter, and so may be varied within wide limits. The chief reason usually given for preferring a small interval, namely, the necessity of keeping within the range where Newton's law of cooling is valid, we have seen to be illusory or trifling (see p. 556). The other main reasons, pro and con, appear to be as follows: In favor of the *large calorimeter* are the reduction in the relative importance of all masses of metal, etc., the smaller part played by evaporation where the temperature rise is small, and the decrease in the cooling constant. This decrease, however, is only proportional to the cube root of the accompanying increase in size, and is therefore not as important as might at first seem. But the accompanying small interval has the advantage of reducing some corrections, such as those of sections 6 and 7 in the preceding paper, and is also almost necessary for the important procedure described in paragraph (*g*) below. In favor of the *large interval* are, first and chiefest, the (often proportional) increase in thermometric accuracy, the diminished importance of the heat of stirring, and the greater tolerance of irregularities in jacket temperature. An increase of the temperature interval to 10° ought not, ordinarily, to augment any error appreciably, and is therefore decidedly advantageous wherever the thermometric error is important, as it nearly always is. If, however, high thermometric precision can be secured without paying too high a price, it can well be used to gain the advantages of the small interval and large calorimeter.

(*e*) *Size of the Air Space Around the Calorimeter Within the Jacket.*—In connection with the experiments on the air lag (p. 571), an unexpected result was found for the effect of air space on the

magnitude of the cooling rate. One of the square cans, at room temperature and carefully shielded on all but one side, received heat through that side from a warmer can whose distance from it was varied. The rate of heat flow across an air gap of 5 mm. was found to be three times as great as across a 15-mm. gap. No significance is to be attached to the exact value here obtained, but the general result, that the cooling rate is very much greater for a small gap, is important. For the only object of a small gap, ordinarily, is to diminish uncertainties due to the air, and these have been shown (p. 572) to be nothing but a very small time lag. But with the cooling rate much increased, the temperature effect of a given time lag also increases. The small gap thus defeats its own object, unless the time lag at the same time decreases greatly, which is unlikely. Moreover, even if the already negligible lag were completely eliminated, the gain would not be appreciable, while the increase in the cooling rate is a real disadvantage. It appears, therefore, that the loose jacket already recommended on account of evaporation (p. 551) is also preferable on other grounds. Apparently, the intervening distance should be from 1 to 2 cm. if not more. Very likely there is a distance for which the cooling is a minimum. Further investigation seems desirable here.

(*f*) *Use of Slowly Evaporating Fluids in Place of Water.*—Other fluids than water have sometimes been used, to reduce evaporation. Their use in the same calorimeter increases (usually about doubles) the *direct* cooling, but on the view presented above, that the most serious difficulties in the cooling are due to evaporation and not to direct cooling, they still have a considerable advantage. The use of fluids of low specific heat merely to increase the temperature interval is, aside from evaporation, somewhat less advantageous than the use of a smaller calorimeter with water, on account of the larger cooling rate.

(*g*) *Making the Final Temperature near that of the Jacket.*—Three advantages may be secured when the calorimeter is started at a relatively low temperature, so as to end near the jacket. (1) The total value of the cooling correction may be brought indefinitely near to zero. This ancient device is (according to the conclusions of the present article) well-nigh useless as far as concerns its original

object, the diminution of the cooling correction error through a decrease in the magnitude of the correction itself. It is, however, of high value if used to increase accuracy (or, at any rate, speed) by avoiding the necessity for running any cooling period, as explained in section 1, *c*, page 577. (2) The final cooling *rate* may be brought indefinitely near to zero. This is of some advantage in specific heat determination where large, poorly conducting bodies are dropped into the calorimeter, since it insures that the final temperature of the body shall be uniform and equal to that of the water. (3)[1] If the temperature of the calorimeter is always kept below that of the jacket, evaporation becomes very slight. This, as explained in section 1, *a*, page 574, may often be of advantage where the use of a tight cover is inadmissible or inconvenient.

The reduction in the cooling correction is, of course, most complete for a final temperature somewhat above the jacket, but will often be satisfactory for the lower temperature which also prevents evaporation.

Obviously, if the calorimeter is to be at any time cooler than the jacket, the greatest care must be taken to avoid even traces of moisture anywhere inside the jacket, and the lowest initial temperature must be safely above the dew point (see p. 515). Hence this method will generally preclude a very large temperature range, unless the jacket is kept above room temperature. But the advantages of the method will often justify a warming of the jacket, or even an increase in thermometric sensitiveness, if that is necessary to secure the required accuracy along with a moderately small interval.

3. *Special Methods.*

No attempt is made to have this section complete.

(*a*) *Adiabatic Methods.*[2]—In these methods the cooling correction is nearly or quite eliminated by so changing the temperature of the jacket as to keep it always equal to that of the calorimeter. But the error of the cooling correction is negligible if proper precautions

[1]The mention of this consideration was suggested by Dr. H. N. Dickinson, of the Bureau of Standards.

[2]T. W. Richards and others, *loc. cit.*; also Proc. Amer. Acad., *42*, 573, 1907; Jour. Amer. Chem. Soc., *31*, 1275, 1909. F. G. Benedict and H. L. Higgins, Jour. Amer. Chem. Soc., *32*, 461, 1910.

are taken; it is therefore to be expected that the important advantages of these methods will be incidental, or will lie in the direction of convenience rather than accuracy. This view is fully in accord with the facts so far.[1] The adiabatic work already published, however, has all been done with mercury thermometers for rather small intervals, and is not nearly accurate enough to show whether the slight cooling correction errors have been diminished or not. The improvement in accuracy actually shown by this work over previous results with mercury thermometers seems accounted for, first, by the general excellence of the work and second, by an incidental feature, the use of a completely inclosing jacket, whose temperature is uniform and measured. The uniformity and definiteness of this temperature are more important than the particular values given to it. It is significant that the present reported accuracy of the "Harvard adiabatic" method was not reached till the complete inclosure was adopted.

Originally, an important reason for the adiabatic method was thought to lie in the avoidance of lag errors, but these have since been shown to be non-existent or easily avoidable in other ways.[2]

There remain several very small possible errors, such as that from the effect of the air in the jacket, which may have to be reckoned with in work of the highest precision, but it is now too early to say whether these errors on the whole are less or greater with the adiabatic method. In either case, however, the adiabatic will have value as an alternative method, to use in connection with others so as to avoid possible systematic errors. It seems also decidedly useful in protracted determinations. Otherwise, its advantages seem to be in convenience, due mainly to the avoidance of the cooling correction calculations. Against this saving, however, must be set a need for additional manipulation, and if a comparison is made with rapid methods such as those of the preceding paper, instead of with some of the older and more tedious procedures, the advantage of the adiabatic method is not so striking. The method of sec. 2, *g*, in this paper (pp. 577 and 582) seems more gen-

[1]Compare also T. W. Richards and R. H. Jesse, Jr., Jour. Amer. Chem. Soc., *31*, 269, 1910.

[2]The constant temperature during final readings in the adiabatic method tends to increase accuracy with *mercury thermometers*, as Richards has pointed out.

erally convenient than the adiabatic. In convenience, then, as well as in accuracy, the adiabatic methods seem most properly classed as valuable alternative methods, whose employment in place of others will depend upon circumstances, perhaps often upon individual preference.

(*b*) *The Use of a Vacuum Jacket* (*Dewar Flask*).—With a vacuum jacket the cooling rate, and with that the requirements as to timing and stirring, and most lag effects, is diminished without any extra manipulation. Hence, while the errors avoided are not the most important, the method is clear gain wherever its special disadvantages are not too severely felt. These are, fairly obviously, the restrictions imposed by the form and brittleness of the flask itself, the lag of the glass parts *above* the water, and the greater difficulty of finding the heat equivalent, of keeping that constant, and, perhaps, of controlling evaporation.

(*c*) *The Use of Large Temperature Intervals.*—The mere use of a large interval (sec. 2, *d*, p. 580) is not, strictly, a distinct method, nor is it new. But it seems to deserve a place here because in diminishing errors it is comparable with the method just mentioned. Its effect, indeed, is generally greater, for it reduces the most important error of all, that in the temperature measurement.

(*d*) *The Comparison Body.*—For the same reason the comparison body (sec. 8, p. 558) deserves mention, though in strictness it is a thermometric as much as a calorimetric device. Its principal advantage is the reduction in the E.M.F. to be measured. This essential feature has been secured in a somewhat different way by A. Magnus,[1] who used instead a duplicate calorimeter within the same jacket. There appear to be cases where this method would be preferable, but the permanent comparison body seems, in the long run, more convenient and less liable to error. It was actually devised as an improvement on an earlier scheme very similar to Magnus's. (I had not then seen Magnus's paper.)

SUMMARY.

1. In calorimetry, the error from thermometric lag is rigorously zero for the assumptions usually made as to the lag of the thermometer, as long as one thermometer is used throughout.

[1]Ann. d. Phys., 31, 597, 1910.

2. Other lags, in the water, in the metal parts of the calorimeter, and in the surrounding air, are all proportional to the total temperature rise, are wholly or largely independent of the rate of heating, and are, moreover, so small as to be usually quite negligible in any case, at least if the "two-temperature system" is used, in which bodies not at the temperature of either calorimeter or jacket are, as far as possible, excluded from the calorimeter chamber.

3. The real sources of error lie in (1) temperature measurement; (2) lack of uniformity in temperature, especially of the jacket; (3) variation in the heat of stirring; (4) variation in evaporation.

4. Of these, (1) is the most serious. An increase in the temperature interval diminishes it proportionately; and such increase is at present one of the most effective methods available for increasing accuracy.

5. Complete avoidance of (2) requires the two-temperature system—that is, absence of large projecting masses, a calorimeter cover in contact with the water, thorough stirring of the jacket water, and a complete inclosure by the jacket.

6. Appreciable error from the heat produced by stirring can always be avoided. In some cases this may require a governor for the stirrer, but usually it will not. The heat increases about as the cube of the speed, hence an unnecessarily high speed is very detrimental. The error is probably less for small calorimeters. The opinion that propellers give more heat than reciprocating stirrers, for the same efficiency, needs reëxamination.

7. Evaporation from the calorimeter water can be made regular within a complete inclosure, if this is not too small.

8. With proper precautions, the cooling correction, contrary to common opinion, is not at present an appreciable source of error.

9. Special methods which aim to increase accuracy by diminishing the cooling correction are, therefore, not likely to be very effective, though they may be convenient.

10. The advantages of a number of methods and variations in procedure are also discussed in the paper.

GEOPHYSICAL LABORATOTY,
CARNEGIE INSTITUTION OF WASHINGTON,
WASHINGTON, D. C., July 15, 1910.

THE MOLECULAR AND THE FRICTIONAL FLOW OF GASES IN TUBES.

DISCUSSION BY MARTIN KNUDSEN AND WILLARD J. FISHER.

IN reply to Mr. Willard J. Fisher's remarks[1] about the importance which the mercury vapor might have had to the result of my experiments[2] on the flow of gases through narrow tubes at low pressures, I beg to state the following:

An easy calculation shows that the wall of tube no. 4 has an inner surface about 5,000 times as large as the sum of the transverse sections of all the mercury molecules together in the tube. It therefore is difficult to see how the mercury vapor can to any extent worth mentioning influence the purely molecular flow. Accordingly as mentioned in my paper (*l. c.*, p. 89), I have not regarded the presence of mercury vapor as a satisfactory explanation of the fact that the quantity of gas passing through the tube is diminished at increasing mean pressure, reaches a minimum, and then goes on to increase. In my experiments with carbonic acid, tube no. 4, this minimum is reached as a partial pressure of the carbonic acid as high as 0.3 mm. mercury pressure, whereas the pressure of the mercury vapor at the experimental temperature of 25° is only 0.00181 mm.[3] The explanation therefore given in my papers seems to me more natural viz., that the first effect of an increase of the partial pressure of the gas, without the alteration in the pressure difference, must be that the gas molecules interfere with one another's passing through the tube, so that the resistance thus caused cannot be compensated for at rather low pressures by the regular movement of the molecules (Poisseuille's flow). It seems to me therefore that just as it would be erroneous to ignore the mercury vapor in frictional experiments with swinging plates, so

[1] Willard J. Fisher, PHYS. REV., Sept., 1909, p. 325.
[2] M. Knudsen, Ann. d. Physik, 28, p. 75, 1909.
[3] M. Knudsen, Ann. d. Physik, 29, p. 179, 1909.

it has been correct to look for other explanations of my experiments on the flow through narrow tubes.

MARTIN KNUDSEN.

KØBENHAVNS UNIVERSITET,
Juni, 1910.

WITHOUT going into great detail I may say in rejoinder to Mr. Knudsen's reply, that my statement about the position of the minimum of the point in question might have been better worded if I had written "The curve for CO_2 shows a decided minimum in the region where *p begins to be* comparable with the saturation pressure of mercury vapor." From that point the curve rises till values of p ranging from 0.004 to 0.0002 mm. are reached; in this range, which included the saturation pressure 0.00181, the observed values of the ordinate are irregular about 0.035. A similar fact shows itself in all the elaborate tables of data; the observed values of T (the ordinate) pass through a minimum as p begins to be comparable with the saturation pressure of mercury vapor, and become irregularly constant for values on either side of this saturation pressure. It is not as easy to explain this relation by the elaborate theory of the paper as by the increasing density of mercury vapor in the tube as compared with that of the gas under experiment. The addition to the Meyer-Bestelmeyer formula which Mr. Knudsen proposes can only be justified by the use of an apparatus in which mercury vapor is excluded from the tube.

I have found the theory of the paper difficult in several points. To give two examples: on page 110 we find the equation

$$G = \frac{\sqrt{\rho_1}}{W}(p_1 - p_2)\,\frac{1}{1 + \dfrac{G}{A^2 W\sqrt{\rho_1}}\,\dfrac{p_1 p_2}{p_1 - p_2}},$$

in which G (page 107) denotes the mass of gas passing the cross-section of the tube per second. In this put p_2 (the exit pressure) $= 0$. Then $G = 0$; in other words, no gas would flow through the tube into a vacuum.

On page 113 the factor $e^{-l/(\lambda \cos \psi)}$ is placed equal to 1, and the expression in which it occurs is then integrated. Now the extreme values of this factor within the range of integration are 0 and 1,

and it cannot be assumed to have a mean value 1 without further demonstration.

In my previous note on this subject[1] the left-hand member of the equation should be pF; page 326, eighth line from bottom, 1 and c_1/c_2 should be interchanged.

WILLARD J. FISHER.

CORNELL UNIVERSITY.

I AM most thankful to Dr. Fisher for the kind interest he has taken in my paper, but I fear that I shall not be able to accept Dr. Fisher's views of the influence of mercury vapor before they are proved by experiment.

With regard to the equation page 110, I may say that the absurdity $G=0$ caused by putting $p_2=0$ does not mean that no gas would flow through the tube into a vacuum bulb, but shows only that it is impossible to have the pressure equal to 0 in any part of a cylindrical tube through which gas is flowing.

The reason why the factor $e^{-l/(\lambda \cos \gamma)}$ on page 113 is placed equal to 1 before the integration in understood when considering the physical meaning of the integration. Put instead of the upper limit $l=\infty$ a value which is great compared with the diameter of the tube but small compared with λ, and try the integration from 0 to this limit and from this limit to ∞.

MARTIN KNUDSEN.

[1] PHYS. REV., 29, p. 325.

ON THE DEFINITION OF A PERFECT GAS.

REMARKS ON THE PAPER OF A. G. WEBSTER AND M. A. ROSANOFF.[1]

BY G. BAKKER.

THE authors consider the following three equations:

$$pv = f(T), \tag{1}$$

$$T\left(\frac{dp}{dt}\right)_v - p = 0, \tag{2}$$

$$T\left(\frac{dv}{dt}\right)_p - v = 0, \tag{3}$$

and demonstrate that each of these three equations is a consequence of the other two. Allow me to point out that in my paper entitled "Connection between the laws of Boyle (Mariotte), Gay-Lussac, and Joule. I"[2] I have treated the same subject and arrived at the same result as Webster and Rosanoff. In the above mentioned paper I observe that the equations (2) and (3) are identical respectively with:

$$pv = f_1(T), \tag{1}$$

$$e = f_2(T), \tag{2}$$

$$e + pv = f_3(T). \tag{3}$$

From these equations I conclude "from this it is immediately evident that each of the three equations is a consequence of the other two." Thus I had already found in 1894 the relation deduced by Webster and Rosanoff in 1909.

I should like to call attention at the same time to my second paper: "Connection between the laws of Mariotte, Gay-Lussac, and Joule. II"[3] in which I have deduced the relation between the depar-

[1] PHYS. REV., 29, pp. 304–309, 1909. Beiblatter zur den Ann. der Phys., No. 11, p. 582, 1910.

[2] G. Bakker, Zeitschr. f. phys. Chem., 14, p. 672, 1894.

[3] Ibid., 17, p. 171, 1895.

tures from the three mentioned laws. These departures I have defined in the following way:

$$\frac{T}{p}\left(\frac{dp}{dT}\right)_v - 1 = \text{departure from the law of Joule,}$$

$$-\frac{T}{v}\left(\frac{dv}{dp}\right)_T - 1 = \text{departure from the law of Boyle,}$$

$$\frac{T}{v}\left(\frac{dv}{dT}\right)_p - 1 = \text{departure from the law of Gay-Lussac.}$$

If now the departures are respectively represented by α, β, and γ I found:

$$\alpha + \beta + \alpha\beta = \gamma$$

and with the aid of this relation I made different observations, among them: If the departures from the laws of Gay-Lussac and Joule are in the same sense, the departure from the law of Boyle is always less than the former, etc.

THE HAGUE, June, 1910.

THE GRATING INTERFEROMETER.[1]

By C. Barus and M. Barus.

1. *Introductory.*—In view of the perfection which has been attained in the construction of film gratings and of the simplicity of the instrumental equipment needed, we have been at some pains to put the type of interferometer recently described[2] into practical form. This is shown in the accompanying diagram of which Fig. 1 is the simplified plan and Fig. 2 the elevation.

The attachment for magneto-striction is purely incidental. The small increments of length in question were thought to offer an excellent test of the availability of the interferometer for micrometric length measurements, when these are of the sudden type and unlike the regular expansions.

2. *Apparatus.*—In Figs. 1 and 2, *A* is the collimator, *B* the telescope for viewing the interference patterns reflected from the grating

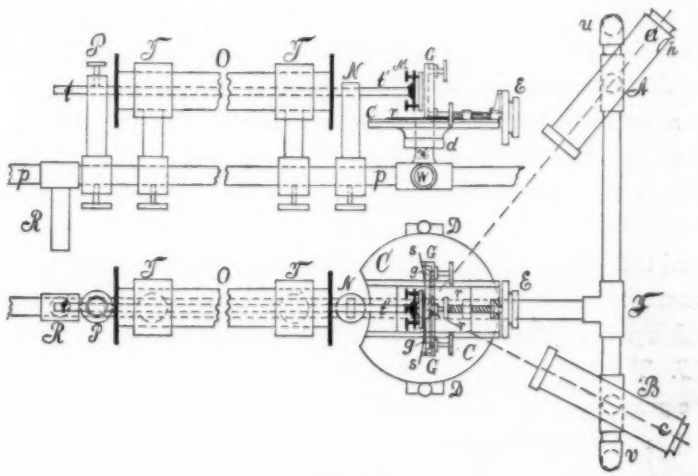

Fig. 1.

[1]From a Report to the Carnegie Institution of Washington.

[2]Science, XXXI., p. 394, 1910; Phil. Mag. (6), XX., p. 45, 1910. Cf. Science, XXXII., p. 92, 1910; Am. Journal Sci., XXX., 1910, Sept.

gg and mirror *M* over the revolvable table *CC*. These are the essential parts. The remainder is the incidental mounting just referred to, *O* being the helix containing an iron rod, soldered at its ends to brass or copper tubes, *t* and *t'*, the latter very light and movable in the *V*-groove *N*; the former *t* heavier and clamped in the upright *P*.

The whole is supported on a frame of quarter-inch gas piping and connections *uFvR*, the feet being at *uvR*, only the latter appearing in the figure. Under the grating is an attachment[1] with four screw sockets *W* at right angles to each other into which a variety of apparatus may be screwed, irrespective of the removable pipe *pp*. When *p* is not used it is replaced by a foot.

Telescope *B* and collimator *A* are carried on *T*-pieces, with nipples at the same height (about 8 cm. or less) above the iron frame and *B* may be slightly inclined about a horizontal axis. It may also be provided with a micrometer eyepiece.

The table *CC* carrying the grating is revolvable on an upright *H* and may be clamped to fixed verniers *D*, also carried at *d* by the upright *H*. The table is cut away on the further side, so that upright apparatus may approach closer to the grating in *GG*. It would even be an advantage to use (not much more than) a semicircular table with verniers *DD* alternately in use, set at an angle.

On the table two parallel brass guides determine the motion of the slide *rr* actuated by the micrometer screw *E*.

The grating is mounted with the film on a glass plate *gg* and exposed on the side away from the observer, facing the mirror *M*. It is adjusted in a rectangular shallow brass case *GG* with the side toward the mirror and the top open. The figure shows three adjustment screws actuating the rear of the glass plate *gg* and the springs *ss* which push the plate to the rear, passing through slits in the sides of *GG*. There is one spring for the top and one spring for the bottom of the grating. The capsule *GG* is firmly attached to the slide *rr* so that the grating may be moved fore and aft by the micrometer screw.

For some purposes the mirror *M*, similarly adjustable by three screws, may be attached to the plate *CC* free from the slide *rr*. In

[1]Usually a special base is provided below *W*.

the figure the mirror is on the light brass tube t' which makes a prolongation of the iron rod, here to be tested for magneto-striction. The silvered face of M fronts the grating.

The coil O used is wound on an annular chamber or double tube (not shown), through which cold water may be kept in circulation to obviate changes of temperature of the rod. The uprights $PTTN$ in Figs. 1 and 2, moreover, are adjustable up and down as well as around the rod pp by suitable clamps.

3. *Adjustments.*—The micrometer screw controlled at E has a double purpose. In the first place it is an immediate check on all measurements of length increment made. It shows, moreover, whether the displacements are expansions or contractions, since it may compensate any motion of the mirror. In the second place since the collimator A and telescope B are at a fixed distance apart approximately in position it enables the observer to put the part of the spectrum needed into the center of the field. For the angle aMc may here be considerably increased or decreased, and both telescopes are slightly revolvable about the vertical. The head E of the screw, moreover, as well as the adjustment screws of the grating are at all times within easy reach of the observer. After an initial rough adjustment (the direct reflections from mirror and grating being put into coincidence), the adjustment screws on the grating are manipulated until the three spectra seen in the telescope B coincide, both horizontally and vertically. For this purpose the D and E lines of the spectrum are useful and sunlight is preferable. In the absence of sunlight a small electric arc lamp with the rays issuing nearly parallel and the carbons impregnated with sodium suffices equally well, even if the apparatus is not in adjustment. When telescope and collimator are fixed, motion at the micrometer screw naturally does not displace the spectrum line λ on which the telescope has been focused, so that the interferences recorded pass through a definite line of the spectrum.

The three sets of interferences available are subject to the equation

$$\delta e'' = \lambda/2 \cos i, \tag{1}$$

$$\delta e' = \lambda/2 \cos \theta, \tag{2}$$

$$\delta e = \lambda/2 (\cos \theta - \cos i), \tag{3}$$

where λ is the wave-length of light used, i and θ the angle of incidence

and of diffraction in air, and where δe, $\delta e'$, $\delta e''$, represent respectively the increment of air space between mirror and grating, per fringe passing the cross hairs. It is therefore necessary to know the angles θ and i, and for this purpose the verniers D and the revolvable plate CC graduated on its edge are provided.

Let the mirror or grating plate be turned until the reflected image of the slit coincides with the slit itself. Here the observer must be able to look at the inner face of the slit in A through the hole h in the tube. Then let the angle be read off. Thereafter let the plate C be unclamped and turned until the slit is seen sharply on the cross wire of the telescope C and a second reading made. The angle so observed is $(i+\theta)/2=a$. We may therefore write

$$\sin i-\sin\theta=2\cos\frac{i+\theta}{2}\cdot\sin\left(\frac{i-\theta}{2}\right)=\lambda/D,$$

where D is the grating space. Thus

$$\sin\frac{i-\theta}{2}=\frac{\lambda}{D\cos a},$$

from which $(i-\theta)/2=b$ may be found. Hence $i=a+b$: $\theta=a-b$. An eccentric position of the grating is of no consequence.

In the given apparatus the inner angle of diffraction has been utilized. This brings A and B closer together for a sufficiently large angle i to secure the best results.

In a later construction on an independent foot under W, uv is a long smooth rod, and A and B are attached by clamps admitting of motion right and left, up and down, and rotation about the horizontal and vertical.

4. *Angular Extent of the Fringes.*—The equations were worked out (l. c.) for the more complicated case of a medium of thickness e and refractive index μ. For the case of an air space the equations become much simplified. Corresponding to equations 1, 2, 3, if $\theta < i$ and $\sin i - \sin\theta = \lambda/D$,

$$\frac{d\theta'}{dn}=\frac{\lambda^2}{2eD}\frac{1}{\cos i\cos\theta}, \tag{4}$$

$$\frac{d\theta''}{dn}=\frac{\lambda^2}{2eD}\frac{1}{1-\sin i\sin\theta}, \tag{5}$$

$$\frac{d\theta}{dn} = \frac{\lambda^2}{2eD} \frac{1}{1 - \cos(i - \theta)}, \tag{6}$$

where $d\theta/dn$ is the angle subtended per fringe for the wave length λ, the grating space D, the thickness of air space e, at an angle of incidence i and of diffraction θ in air.

These three sets need not be in focus at once. Equations 4 and 6 are usually easily put in focus together. Thus in the above case roughly

$$i = 50°24', \theta = 24° 44', \lambda/D = .352$$

whence

$$\lambda = 60 \times 10^{-6} \text{ cm. and } e = 1 \text{ cm.},$$

$$\frac{d\theta'}{dn} = .064', \quad \frac{d\theta''}{dn} = .055', \quad \frac{d\theta}{dn} = .378'.$$

In case of the set of equations 4, 5, 6, therefore, there should be about 6 to 7 small fringes to one large fringe. This is about the order of values usually observed. When e is small the change of wave-length with $d\theta$ must be considered. To obtain a given ratio k of small and large fringe divergences one may write for the cases 4 and 6, for instance,

$$k = 2 \frac{1 - \cos(i - \theta)}{\cos(i - \theta) + \cos(i + \theta)}. \tag{7}$$

Equation 7 is not easily treated. If, however, θ is computed in terms of i and expressed graphically, k may then also be expressed in terms of i; and thus the angle of incidence i for any ratio of size of fringes, k, in question, may be roughly adjusted.

Thus it appears that at $i = 37°$ about, there should be ten small fringes to one large fringe. In a general way moreover the ratio of small to large fringes gives an estimate of the value of i.

Similarly equations 5 and 6 give

$$k' = 2 \frac{1 - \cos(i - \theta)}{2 - (\cos(i - \theta) - \cos(i + \theta))}.$$

The character of k and k' is shown in Table I. In the latter case there will be ten small to one large fringe when i is 40.5°, roughly.

TABLE I.

Ratio of large and small fringes.

i	θ	$1/k$	$1/k'$
0°	−20° 1′	16.4	16.5
10	−10 17	15.6	16.6
20	− 0 34	14.8	15.8
30	+ 8° 31′	12.3	13.3
40	16 54	9.1	10.2
50	24 27	6.0	7.0
60	30 56	3.4	4.4
70	36 0	1.6	2.6
80	39 15	.6	1.5
90	40 24	.0	1.0

5. *The Same, continued.*—The preceding equations 4, 5, and 6 are essentially approximate inasmuch as the rates are taken from finite quantities. If we return to the fundamental equations

$$2e \cos i = n\lambda, \tag{8}$$

$$2e \cos \theta = n'\lambda, \tag{9}$$

$$\sin \theta - \sin i = \lambda/D, \tag{10}$$

for θ greater than i where n and n' are unequal, distributive whole numbers, and if we put $e/D = a$, we find

$$\tan i = \frac{n^2 - n'^2}{4an} - a, \quad \tan \theta = \frac{n^2 - n'^2}{4an'} + a, \tag{11}$$

which are free from λ whereas $\sin i$ and $\sin \theta$ essentially contain λ. As the angular width of a fringe is

$$\theta = \int_n^{n+1} (d\theta/dn)dn,$$

those corresponding to equations 4 and 5 may therefore be expressed as

$$\theta_1 = 2a \int_n^{n+1} \frac{-dn}{n\sqrt{n^2 - 4an \tan i - 4a^2}}, \tag{12}$$

$$\theta_2 = 2a \int_n^{n+1} \frac{-dn}{n(n - 2a \tan i)}, \tag{13}$$

for a given space e in $a = b/D$ and a given angle of incidence i in

tan i. These integrations are easily made, but the results are too diffuse to be worth discussing here. Equation 12, moreover, is a restatement of the fact that in these interferences $n\lambda$ is constant throughout the spectrum.

Equations 8, 9, and 10, however, admit of the graphic treatment of the problem. For if we put $A = nD/2e$, they may be written according as $\theta > i$ or $\theta < i$

$$\sin \theta_1 = \pm \frac{\cos i}{A} + \sin i, \tag{14}$$

$$\sin \theta_2 = \frac{A^2 \sin i \pm \sqrt{1 + A^2 \cos^2 i}}{1 + A^2}, \tag{15}$$

where the distributive number n in A takes the values of the successive whole numbers for a dark band in the respective spectra corresponding to equations 14 and 15. The coincidence of dark bands then determines the position of the coarse fringes.

If $i = 50^\circ\ 24'$, $2e = .1$ cm., $D = .000169$ cm., $\theta = 24^\circ\ 44'$, then $A = .0017 \cdot n$ nearly. With these data tables were computed, which will have to be omitted here. Similar results might be computed for $\theta < i$, but we abandoned it because as is now evident the practical demands are sufficiently met by the method of paragraph 4.

6. *Test Made by Magneto-striction.*—The very small elongation produced when iron is magnetized offers an excellent test of the above apparatus. The attached water-cooled helix has already been described. The rod of Swedish soft iron was quite within the helix which surrounded it closely without contact, the rod being prolonged by light copper tubes soldered to its ends.

A large number of experiments were made for trial, brief examples of which will be given elsewhere.[1] If the current is in amperes the magnetic field was

$$H = 108\, i \text{ gauss}$$

and the elongation $\delta e = 105 \times 10^{-6}$ cm. per large fringe. Thus if

[1]The whole subject which is here touched incidentally is well summarized in Winkelmann's Handbuch, Vol. 5, p. 307 et seq., 1908, by Professor F. Auerbach. Our results agree closely with the elaborate experiments of Nagaoka and Honda who used a special type of contact lever. Recently Mr. Dorsey has made a similar investigation using an ingenious method of his own. (PHYS. REV., XXX., p. 698, 1910.)

n is the number of fringes and $l=28$ cm., the effective length of the iron rod, the absolute elongation is $105n\times10^{-6}$ cm. and the elongation per unit length,

$$\delta\beta = 3.75n \times 10^{-6},$$

or if small fringes N are taken,

$$\delta\beta = .54N \times 10^{-6}.$$

Elongations from 10^{-6} cm. to 10^{-4} cm. were measured without difficulty though such measurement without micrometer attachment is essentially an estimate. The number of small fringes was counted between the large fringes. The present method would not have been feasible, but for the occurrence of large and small fringes in the field of the telescope at the same time.

BROWN UNIVERSITY,
PROVIDENCE, R. I.

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY.

MINUTES OF THE FIFTY-THIRD MEETING.

A REGULAR meeting of the Physical Society was held at Columbia University, New York City, on Saturday, October 15, 1910.

In the absence of the President, Vice-President Magie presided.

The following papers were presented:

The Freezing of Water under High Pressure. P. W. BRIDGMAN.

The Electrical Properties of Selenium. LOUISE S. MCDOWELL.

The Positive Thermions Emitted by the Salts of the Alkali Metals. O. W. RICHARDSON.

Discharge from Hot CaO. C. D. CHILD.

Certain Peculiarities of the Discrepancies among Wave-length Determinations. (Read by title.) IRWIN G. PRIEST.

Spectral Luminosity Curves Obtained by the Equality of Brightness and Flicker Photometers. H. E. IVES.

The Limit of Visibility in the Red. HENRY PHELPS GAGE.

Torsional Rotatory Polarization. A. W. EWELL.

The Scientific Results of the First Cruise of the "Carnegie" in Magnetism, Electricity, Atmospheric Refraction, and Gravity. L. A. BAUER.

Note on Oscillatory Interference Bands and some Practical Applications. GEO. O. SQUIER and A. C. CREHORE.

The Magnetic Effect of Cathode Rays. A. W. DUFF and G. R. OLSHAUSEN.

On the Question of the Motion of the Ether in a Steady Electromagnetic Field. (Read by title.) S. J. BARNETT.

The Action of Mercury on Steel at High Pressures. P. W. BRIDGMAN.

Note on Crová's Method of Heterochromatic Photometry. H. E. IVES.

Gravitation and the Electron Theory. O. W. RICHARDSON.

The secretary made an announcement in regard to an increase in the payment by this Society to the publishers of Science Abstracts for copies of that journal furnished to Physical Society members. Owing to the fact that Science Abstracts has for some years been published at a loss it was found necessary to increase the amount paid by the Physical Society from $1.50 a copy to $2.50 a copy. The Council had authorized this increase for the year 1911, but had postponed the decision regarding any permanent action,

since the continuance of this payment would make necessary an increase in the annual dues of the Society.

Adjourned at 4 P. M.

ERNEST MERRITT,
Secretary.

A NEW METHOD OF MEASUREMENT OF SMALL ANGLES.[1]

BY C. W. CHAMBERLAIN.

THE application of the interferometer to the measurement of small angles is open to the objection that as the sensibility of the instrument is raised by increasing the length of path of the interfering rays, its susceptibility to disturbance from vibration and temperature change increases at a rapid rate. For the determination of small angles the diffractometer, a combination of interference and diffraction systems, possesses a marked advantage, inasmuch as its susceptibility to disturbance does not increase as its sensibility is increased. Straight interference bands are produced by means of an interferometer. The light is allowed to fall upon a grating the lines of which are parallel to the interference bands. In monochromatic light the interference bands appear in the direct illuminated field and in the diffracted images of the field. In white light the interference bands appear in the direct field only when the paths of the two interfering beams are equal. By making one path longer or shorter than the other by an amount depending upon the width of the bands employed and the distance between the interferomenter and the grating, interference bands may be made to appear in the several diffracted images of the field. These bands may be called diffractometer bands to distinguish them for those of the interferometer. When one mirror of the interferometer is rotated about an axis parallel with the lines of the grating the diffractometer bands move in the spectrum. The sensibility of the instrument is raised by increasing the distance between the interference and diffraction systems, while relative motion between these two systems produces no disturbing effect.

NOTE ON "CHANGES IN DENSITY OF THE ETHER AND SOME OPTICAL EFFECTS OF CHANGES IN ETHER DENSITY."[2]

BY CHARLES F. BRUSH.

A BRIEF résumé of the Hanover paper of this title is given, and attention is directed to the wide difference in character of its two divisions. No further investigation has yet been made in the subject

[1] Abstract of a paper presented at the Boston meeting of the Physical Society, December 28–30 1909.

[2] Abstract of a paper presented at the Washington meeting of the Physical Society, April 22–23, 1910.

matter of the first, and principal, division, which deals with radiation of great wave-length. The original conclusions in this connection remain substantially unchanged.

The second division of the Hanover paper, which deals with the short-wave radiation of actinic light, has been the subject of exhaustive investigation which, however, has failed to confirm this portion of the work. The writer concludes that the supposed change in ether density cannot, with certainty, be shown by the photographic method. The photographic effects described in the Hanover paper were largely due to a combination of disturbing factors mostly of photographic origin, some of them obscure and at first unsuspected. These are described at length, and explained, in another paper under the title "Photographic Photometry, and Some Interesting Photographic Phenomena."

Preliminary Report on Temperature Coefficient of Resistivity of Copper.

By J. H. Dellinger.

THE values in use for this constant vary widely, and are based upon but little experimental work. None of these values therefore can be relied upon to give accurate results when applied to any particular sample. The present investigation indicates a simple linear relation between the conductivity and temperature coefficient, so that a measurement of the former gives also the latter for any particular sample. The relation is found to hold for samples of both lake and electrolytic copper, and for both annealed and hard-drawn samples, throughout the range of conductivity of copper now on the electrical market. The relation is in corroboration of a conclusion of Matthiessen's for the pure metals. It may be expressed as follows: The 20° C. temperature coefficient of a sample of copper is given by multiplying 0.00393 by the percentage[2] conductivity. There may be herein an explanation of the disagreements of previous determinations of the temperature coefficient.

It may be noted that the temperature coefficient assumed by the American Institute of Electrical Engineers, 0.0042 at 0° C., or 0.00387 at 20° C., corresponds to a conductivity of 98.6 per cent.; if it were used for a sample whose conductivity is 100.3 per cent. (an average value for the annealed copper of commerce), the error of the computed value at 100° C. would be over one half per cent.

[1] Percentage conductivity is reckoned on the basis of 100 per cent. conductivity corresponding to 0.1530_{22} ohm per meter-gram or 1.721_{28} micro-ohms per centimeter cube at 20° C.

CERTAIN PECULIARITIES OF THE DISCREPANCIES AMONG RECENT WAVE-LENGTH DETERMINATIONS.[1]

BY IRWIN G. PRIEST.

COMPARISONS, inter se, of the published results of the recent wave-length determinations by Fabry and Buisson, Pfund, and Eversheim[2] and of Eversheim's most recent results[3] with the previous values of Michelson, Fabry and Perot, and Rayleigh disclose certain remarkable peculiarities of the discrepancies such as would not be expected to be due to chance (*i. e.*, to irremovable sources of small accidental errors). There is ground for suspicion that these peculiar discrepancies are due to some unrecognized but removable sources of error in some of the measurements. If there are such sources of error, their discovery would, of course, permit of bringing the different results into closer agreement and of making a closer approximation to the true values of the wave-lengths. The definite formulation of these peculiarities might serve as a basis for a working hypothesis to account for the discrepancies, and so might lead to an improvement of the method. Inasmuch as these peculiarities are not at all emphasized in even the most recent publications of the authors of the work in question, it is intended, in this communication, to formulate and present them as they appear to the present author.

Tabulation of the discrepancies among the results[4] of Fabry and Buisson, Pfund, and Eversheim warrants the following conclusions, where the initials and sub cripts refer to the authors and the year of publication:

1. The difference $(F. \& B.)_{08} - P_{.08}$ is not markedly systematic when the whole range of the spectrum covered is considered. Considering the precision of the measures, the systematic difference that does appear is perhaps negligible.

2. Throughout the range of the spectrum from 5,167Å. to 6,495Å., inclusive, the difference $(F. \& B.)_{08} - P_{.08}$ is sensibly systematic, the algebraic mean discrepancy being + 0.0015Å. Out of the total of twelve differences to be considered in this range, only one is negative, viz: — 0.001Å. for $\lambda = 5{,}167$Å., the limit of the range.

3. Throughout the range of the spectrum from 4,282Å. to 5,002Å., the difference $(F. \& B.)_{08} - P_{.08}$ is not *markedly* systematic although there is a

[1]Abstract of a communication offered for presentation at the New York meeting of the American Physical Society, October 15, 1910.

[2]Fabry and Buisson, Jour. de Phys. (4), *7*, 169, 1908; Trans. in Astrophys. Jour., *28*, 169, 1908. Pfund, Astrop. Jour., *28*, 197, 1908; J. H. Univ. Circ., Feb., 1910. Eversheim, Ann. der Phy., *30*, 815, 1909; Table of results, Atsrophys. Jour., *31*, 76.

[3]Zeit. für wiss. photog., *8*, 148, March, 1910.

[4]Astrophys. Jour. *28*, 195; J. H. Univ. Cir., Feb., 1910, pp. 33 and 34; Ann. der Phys., 30, pp. 837–838.

slight predominance of negative values, the algebraic mean discrepancy being — 0.00045Å. Out of the total of eleven differences to be considered, four are positive, five are negative and two are zero.

4. Considering the whole range of the spectrum covered in common by the several investigators, the results of Eversheim appear to be systematically higher than those of Pfund and Fabry and Buisson by about 0.001Å.

5. *The differences,* $(F. \& B.)_{08} - E._{09}$ *and* $P._{08} - E._{09}$ *when grouped according to sign are also grouped in certain spectral regions as indicated in Table I. In the differences* $P._{08} - E._{09}$ *the coincidence of the grouping according to sign and the grouping in spectral regions is pronounced and unmistakable. The spectral grouping of the positive and negative differences* $(F. \& B.)_{08} - E._{09}$ *while less pronounc d than for the differences* $P._{08} - E._{08}$ *is not inconsistent with this grouping, and the tendency of the groups in the system* $(F. \& B.)_{08} - E._{09}$ *to coincide in spectral position with groups of the same sign in the system,* $P._{08} - E._{09}$ *is decided.*

The discrepancies existing between Eversheim's recently published results (March, 1910) and previously accepted values are exhibited in Table II. Inspection of this table leads to the following conclusions:

1. The results of Eversheim are systematically higher than those of Rayleigh, Michelson, and Perot and Fabry by nine times the error corresponding to the desired accuracy in these values and several times the supposed accuracy of these determinations. In the ten wave-lengths to be considered there is no exception to the rule that Eversheim's values are higher than those of other investigators.

2. The departure of Eversheim's value from Michelson's for the blue cadmium, amounting to one part in 370,000 is more than 50 times the uncertainty assigned by Michelson to his determination. In this connection it should be noted that Rayleigh, by a method identical with Eversheim's in fundamental principle but differing in details of experiment, has checked[1] Michelson's value to one part in 2,000,000.

3. The discrepancies are so large in comparison with the accidental errors of measurement as to make it almost certain that either Eversheim's values are systematically higher than the true values or Michelson's, Perot & Fabry's, and Rayleigh's are all systematically low.

In summary, we have then the following facts requiring explanation:

1. The tendency of Fabry and Buisson's values to be higher than Pfund's for wave-lengths greater than 5,000Å.

2. The slight but perceptible tendency of Eversheim's values of the iron wave-lengths to be higher than those of the other investigators.

3. The grouping of differences of like sign in certain spectral regions in the discrepancies between Eversheim and Pfund, and to a less degree in the discrepancies between Eversheim, and Fabry and Buisson.

[1]Phil. Mag. (6) *11*, p. 700; 1906.

4. The very pronounced systematic difference between Eversheim's recent determinations of the helium, mercury yellow and cadmium blue wave-lengths and previous determinations of the same wave-lengths by other investigators.

TABLE I.[1]

Group.	$(F. \& B.)_{08} - E._{09}$.						$P._{08} - E._{09}$.					
	Limits of Group.	Number of Lines in Group.	Distribution of Differences According to Sign.			Algebraic Average of Differences.	Limits of Group.	Number of Lines in Group.	Distribution of Differences According to Sign.			Algebraic Average of Differences.
			+	o	−				+	o	−	
I.	4,282 4,593	9	4	3	2	0.0000	4,282 4,494	5	5	0	0	+0.0016
II.	4,603 5,083	16	1	1	14	−0.0022	4,860 5,002	5	0	0	5	−0.0020
III.	5,110 5,456	10	5	3	2	+0.0016	5,167 5,456	4	3	0	1	+0.0022
IV.	5,498 6,495	17	3	5	9	−0.0014	5,498 6,495	8	0	0	8	−0.0038

TABLE II.[2]

λ (Helium.)	$R._{08} - E._{10}$
7065	−0.010Å
6678	− 4
5876	− 16
5016	− 5
4922	− 6
4713	− 12
4471	− 13
(Cadmium.)	$M._{05} - E._{10}$
4800	−0.013
(Mercury.)	$(F. \& P.)_{99} - E._{10}$
5791	−0.007
5770	− 7
Algebraic average of above ten differences	−0.0093

[1]Data from sources cited in footnote 4.

[2]Data from: Zeit. für wiss. photographie, *8*, p. 150, 1910. Perot & Fabry, Ann. de Chim. et de Phys. (7), *16*, p. 320, 1899. Rayleigh, Phil. Mag. (6) *15*, p. 549, 1908. Michelson, Trav. et Mem. Bur. Int., *11*, p. 85, 1895. The older values, viz.: those of Perot and Fabry, Michelson, and Rayleigh have been reduced to the recent definition of the Ångström Unit [*i. e.*,

$$1\mathring{A} = \left(\frac{\text{wave-length of red cadmium light}}{6{,}438.4696}\right)]$$

which is used by Eversheim.

The initials refer to authors and the subscripts to year of publication.

Discharge from Hot CaO.

By C. D. Child.

IT was suggested a few years ago by Sir J. J. Thomson,[1] that certain phenomena could be explained by what we may call ionization by *repeated* impact. He had found that luminous discharge could be produced from hot CaO with much smaller potential differences than those needed when a cold cathode was used and that at a certain critical point it needed but a small increase in the potential difference to cause a very great increase in the current and to change from a non-luminous to a luminous discharge. He believed that the ionization in the luminous discharge was not due to a breaking up of the atom by a single impact of an electron, but rather to an explosion of the atom because of its having absorbed so much internal energy from repeated impacts of electrons that its equilibrium had become unstable

If this idea is correct, it is important not only because it gives us information concerning the character of the atom, but also because it offers an explanation of the ionization of the arc. I have, therefore, given some study to the phenomenon and find several reasons for rejecting the suggestion made by Professor Thomson. These are as follows:

First, the scarcity of electrons present in the tube before luminous discharge commences renders repeated collisions very improbable. With the largest current which could be used without producing luminous discharge in one of the cases examined, the molecules were hit by electrons only once in three hours, while the time needed to start the luminous discharge was only a fraction of a second.

Second, we find from experiment that the potential difference at which the the sudden change occurs depends far more on the kind and temperature of the cathode than on the amount of current flowing through the arc. In other words the number of collisions which may take place between the electrons and the molecules of the gas has little, if anything, to do with the change from the non-luminous to the luminous discharge.

Third, the electrostatic effect of the positive ions moving toward the cathode would be more than sufficient to reverse the direction of the field, if the increase in current were produced by increased ionization of the gas without there being also an increase in the number of electrons leaving the cathode.

The phenomena can, however, be easily explained, if we assume that the positive ions hitting on the surface of the cathode can ionize much more easily when the cathode is hot than when it is cold. Such an assumption is quite in harmony with the work which has been done by others and with experiments performed by myself on the discharge from hot CaO. Such an assumption would also explain the comparatively small cathode drop of the electric arc.

[1] Nature, 73, 496, 1906.

THE FREEZING OF WATER UNDER HIGH PRESSURE.[1]

BY P. W. BRIDGMAN.

IT is well known that the effect of pressure on the ordinary modification of ice is to depress the freezing point, this being a thermodynamic consequence of the fact that ice is less dense than water. Tammann, however, has shown that at $-22°$ and 2,200 kgm. per sq. cm. the ordinary modification of ice becomes unstable, giving place to a modification more dense than water, the freezing point of which is consequently raised by the application of pressure. Tammann followed this freezing curve up to about 3,300 kgm., and predicted that there would be found a maximum freezing temperature at nearly $-16°$ and 5,000 kgm.

In the present work water has been found to change its form at room temperatures if the pressure is sufficiently high. The freezing curve has been followed by measuring under pressure the electrical conductivity of water made very slightly conducting, the depression of the freezing point so introduced being negligible. Freezing is shown by sudden increase in the resistance. The curve has been followed from $+24°$ and 11,000 kgm. per sq. cm. to $-5°$ and found to be linear. On this line the pressure corresponding to $-22°$ is 2,500 kgm., being therefore higher than Tammann's value. Whether this is the same modification of ice as that found by Tammann has not yet been verified.

THE ACTION OF MERCURY ON STEEL AT HIGH PRESSURES.[1]

BY P. W. BRIDGMAN.

IT has been found impossible to retain mercury in steel cylinders at high pressures, the cylinder bursting at about one sixth the normal bursting pressure, when the fluid is water. This bursting is not due to penetration of mercury hrough the pores of the steel, but is due to amalgamation of the steel. It was furthermore shown that there is at atmospheric pressure very strong tendency for mercury to amalgamate iron, as is proved by the amalgamation produced by rupturing steel under a mercury surface. In all cases in which bursting has been produced by mercury under pressure it was shown that there are two agencies acting together to produce this effect: the natural tendency for mercury to amalgamate iron, and the action of the stress, which must be in such a direction as to produce volume dilation, opening up the pores for the entrance and amalgamation by the mercury. A piece of iron submerged beneath a mercury surface and subjected to hydrostatic pressure shows no amalgamation.

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[1]An abstract of a paper read before the New York meeting of the Physical Society, October 15, 1910.

The Limit of Visibility in the Red.

By Henry Phelps Gage.

WHEN measuring the radiant efficiency of a light either by the method of integrating the energy curve or by the method of Ångstrom it is necessary to assign arbitrarily certain wave-lengths as the limits of visibility in the spectrum. The limit usually chosen in the red is the A line .76μ. This point is far beyond the apparent end of a continuous white light spectrum. Looking at a continuous spectrum and setting the cross hair of the spectroscope on the red end will give a value of from .68μ to .71μ according to circumstances.

Several "visibility curves" found in the literature were studied and some new observations were made by the author. These curves were used to compare the illumination due to the entire spectrum with the illumination due to light of wave-length greater than certain values. The results were plotted in curve form and showed that the illumination due to light of wave-length greater than .68μ is less than 1.6 per cent. of the total illumination of the spectrum. This value 1.6 per cent. is the minimum difference in illumination of two adjacent patches of light which can be detected.

.68μ was chosen as the limit of the spectrum for work on radiant efficiency. It is easily located in the arc spectrum of a mixture of potassium and lithium. being slightly less than half way between the lithium line .671 and a potassium line .691.

The exact location of the limit of visibility in the blue is of little importance for purposes of measuring radiant efficiency as no light source has much energy in this part of the spectrum.

Torsional Rotatory Polarization.

By A. W. Ewell.

IT has been shown in previous papers[1] that:

1. Rotation of the plane of polarization occurs when plane polarized light traverses a twisted jelly cylinder parallel to the axis, and the direction of this rotation is opposite to the direction of the twist.

2. The rotation is independent of the distance of the path from the axis.

3. The rotation produced by a jelly cylinder is increased by inclosing the cylinder in a tightly fitting rubber tube.

4. Hydrostatic pressure has no influence.

5. Longitudinal compression of a rubber-covered jelly cylinder increases the rotation for a given twist, the law being approximately $\log \theta = A + Bx$, where θ is the rotation, x the compression, and A and B are constants.

[1]Am. Jour. of Science, 1899, VIII., p. 89; 1903, XV., p. 363. Phys. Zeit., 1899, p. 201; 1903, p. 706; Johns Hopkins Univ. Circular, 1900, p. 64.

6. The rotation is proportional to a high power of the twist (approximately fou th power).

This phenomenon has been further studied during the past year and the following additional results have been obtained.

Other conditions being equal, the rotation produced by a twisted, rubber-covered cylinder is approximately:

7. Proportional to the square of the diameter.

8. Inversely proportional to the square of the length.

9. Inversely proportional to the square of the wave-length of the light employed.

When such a cylinder is twisted, the cross section becomes an ellipse and the ellipticity increases with the twist, with the diameter, and with longitudinal compression. Other conditions being equal, the sum of the proportional changes in the two diameters is:

10. Proportional to a high power of the twist.

11. Approximately proportional to the diameter.

12. Increases rapidly with longitudinal compression.

13. Both bare and rubber-covered jelly cylinders of initial elliptical cross section show much greater rotation when twisted than similar cylinders with initial approximately circular cross sections.

14. If an initially approximately circular jelly cylinder is constrained by an external, circular metal envelope to conserve the circular cross section, the rotation is very small and does not increase upon increasing the twist.

The last two facts suggest that the rotation is due to the double refraction caused by the change in cross section and the helical arrangement of the axes of this double refraction. Upon this basis and Mallard's analysis of the optical properties of piles of double refracting plates a theory of the phenomenon has been constructed. The relations be ween rotation and twist, length, diameter and wave-length required by the theory agree reasonably well with the experimental results.

THE POSITIVE THERMIONS EMITTED BY THE SALTS OF THE ALKALI METALS.[1]

BY O. W. RICHARDSON.

THE paper describes the results of measurements of the value of e/m for the positive ions emitted by the salts of the alkali metals when heated. The method was the same as that already used by the author to measure e/m for the positive ions emitted by hot metals. The salts experimented on were melted in a thin layer over a platinum strip whose power of producing positive ionization had been destroyed by previous heating.

[1]Abstract of a paper presented at the New York meeting of the Physical Society, October 15, 1910.

The values of e/m are found to be inversely proportional to the atomic weights of the metallic elements present in the compounds used. If we assume that these ions carry the same charge as an atom of hydrogen in electrolysis then the experimental values of the masses of the ions, in terms of the mass of the hydrogen atom as the unit of measurement, were found to be: for Li_2SO_4: 6.2, Na_2SO_4: 22.5, K_2SO_4: 36.5, Rb_2SO_4: 96 and Cs_2SO_4: 40. The atomic weights of the alkali metals are: Li = 7.05, Na = 23.05, K = 39.15, Rb = 85.5 and Cs = 132.9. The experimental values agree with the atomic weights of the metals within the limits of accuracy of the method of measurement.

In the case of lithium sulphate the true value of e/m is only obtained after continued heating. This is due to the presence, in ordinary pure lithium sulphate, of compounds of the alkalis of higher atomic weight, which are more volatile and are also more efficient as emitters of positive thermions.

Separate experiments were made on the following compounds of sodium: Na_2SO_4, NaF, and NaI. All of these gave the same value of e/m, showing that the nature of the ions depends only on the metal present.

The results of the experiments prove that the positive ions emitted by the salts of the alkali metals when heated are atoms of the constituent metal carrying a charge equal to that of the electrolytic hydrogen ion.

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GRAVITATION AND THE ELECTRON THEORY.[1]

BY O. W. RICHARDSON.

IN the last two decades the electron theory has been extraordinarily successful in explaining practically all of the phenomena dealt with in the exact sciences, with the exception of gravitation. It is very important to determine whether gravitation lies outside the scope of the electron theory or not. This attitude has already been adopted by H. A. Lorentz and Sir J. J. Thomson. Lorentz has established the very important conclusion that if gravitational effects are propagated through space according to the same laws as electrical actions the results could not be distinguished, by their influence on astronomical data, from those which follow from the usual Newtonian theory. If gravitational action is propagated, it would appear to follow that its velocity cannot exceed that of light from the principle of relativity, according to which the velocity of light is the greatest velocity possible.

This paper presents the case for the view that gravitation is an electrical

[1]Abstract of a paper presented at the New York meeting of the Physical Society October 15, 1910.

effect at bottom but that it occurs in such a way that the Newtonian law

$$F = k\frac{mm'}{r^2}$$

is true for neutral elements of attracting matter, however small they may be. The argument may be briefly summarized as follows:

The following propositions are assumed to be justified by experiment:

1. Mass is a property of electric charge which depends on the distribution and velocity of the charge.

2. The number of electrons in the atom is a quite small multiple n of the atomic weight.

3. The numerical values of the atomic weights differ from integral multiples of $1/n$ by an amount which exceeds the errors of experiment.

4. The law that the ratio of weight to mass is independent of the chemical nature and physical state of the substance is either exact, or at any rate, very nearly so.

These propositions make it highly probable that the mass of matter is the mass of the electric charges it contains. The alternative is that practically the whole of the mass of an atom is non-electro-magnetic. We cannot absolutely deny this possibility, but the trend of current discovery is against it. On such a view there would be no definite reason to expect approximate proportionality between the atomic weights and the number of electrons in the atom. There is also the a priori argument that it leaves us with two kinds of mass, one accounted for by electrical theory and the other unexplained, and that it would be a unique phenomena outside of the scope of electron theory.

Admitting the theorem that the mass of a material particle is the mass of the electric charges it contains, we should expect as a first approximation that the atomic weights would be proportional to the number of electrons the atoms contain. This will only be exact so far as the mass of an electron does not vary from one atom to another. Our interpretation of proposition (3) is that such variation does occur.

It follows from this conclusion combined with proposition (4) that we cannot derive the law of gravitational attraction by simply multiplying the ordinary expressions for the force between electrons by a constant quantity different for each kind of pair of electrons considered. Such an assumption will only lead to the Newtonian law of gravitational attraction provided that the mass of an electron does not vary from one atom to another. It is necessary that the deviation from the ordinary law of electrostatic action should be dependent for each element of charge upon the element of mass associated with that charge; and in such a way that the differential effect arising from equal and opposite charges is proportional to the sum of the masses of the charges.

These conditions are satisfied if the repulsion between two elements δE, $\delta E'$ of electric charge is of the form:

$$\frac{\delta E \delta E'}{r^2} F\left(\frac{dM}{dE}, \frac{dM'}{dE'}\right) = \frac{\delta E \delta E'}{r^2}\left[1 + a\frac{dM}{dE} + b\frac{dM'}{dE'} + c\left(\frac{dM}{dE}\right)^2\right],$$

where dM and dM' are the infinitesimal amounts of mass associated with dE and dE' respectively, a, b, c, d, and e are constants, and F denotes some functional relation. A formula of this type might be expected to arise if the usual law of force were modified to a slight extent by the disturbance in the ether in the immediate neighborhood of the element of charge, since, according to certain forms of electrical theory, the mass of any region is proportional to the energy confined in that region.

The constant a does not enter into the expression for the force between two neutral particles. They would, however, make a difference in the effect of gravity on an electric charge. Experiments on electrons may possibly indicate such a difference. There seems to be no reason why gravitation should not act differentially on opposite charges. An action of this kind might account for the magnetic fields of the earth and the heavenly bodies.

The Scientific Results of the First Cruise of the "Carnegie" in Magnetism, Electricity, Atmospheric Refraction, and Gravity.[1]

By L. A. Bauer.

THE first cruise of the "Carnegie" began at Brooklyn in August, 1909, and ended at the same place in February of the present year. During this period of about six months, a total distance of 8,000 nautical miles was covered in the North Atlantic Ocean between the parallels 51° north and 19° north and the following ports were visited: Greenport (Long Island), St. John's (Newfoundland), Falmouth (England), Funchal (Madeira), Hamilton (Bermuda) and Brooklyn (New York). Last June the vessel started out once more, this time on a circumnavigation cruise of 65,000 miles to extend over a period of three years and to embrace the Atlantic, Indian and Pacific Oceans; she has already completed a voyage of nearly 7,000 miles to Para at the mouth of the Amazon River. The present voyage has not only cut across our first cruise, but is so arranged, by the introduction of loops, as to intersect itself also at various points. We are thus enabled to apply numerous checks.

In addition, special observations have been made in Gardiner's Bay, off Long Island, and on the neighboring islands at the beginning of the first cruise in September, 1909, and again at the beginning of the present cruise

[1]Abstract of a paper presented at the New York meeting of the Physical Society, October 15, 1910.

in June of this year. The results of all these elaborate tests have shown conclusively that, with a non-magnetic vessel like the "Carnegie" and with the instrumental appliances and methods used, it is possible to secure an accuracy in the magnetic results approaching that of land observations.

As I am to cover four lines of activity on this vessel in the space of a quarter of an hour, it will not be possible to go into further detail and I will have to content myself with stating at once the main conclusions reached.

A. *Terrestrial Magnetism.*—Except for the portion of the cruise from 48°.5 N., 47° W. to Falmouth Bay and thence to Madeira, all charts show too low west magnetic declination over the portion of the Atlantic Ocean covered by the "Carnegie." While the correction is in general less than a degree, it is unfortunately in the same direction for about 5,000 miles, and hence the resulting error in a ship's course based on the present mariners' charts may be accumulative and ultimately reach a considerable amount. The maximum chart error at any one point may be from 1°.3 to 2°.6 according to the chart used.

The chart corrections both for magnetic inclination and horizontal intensity, often being of opposite signs on the portion of the "Carnegie" cruise given, the average algebraic correction is in consequence at times greatly reduced. The average chart correction (sign not being considered) for magnetic dip approximates 1°.5 to 2°; the maximum correction for the British chart is 2°.5 and that of the German, 4°.4. It is also seen from the values of the average algebraic dip correction, that the British chart gives, in general, too small dips and the German too large ones. The average chart corrections for magnetic horizontal intensity, disregarding sign, approximate 8 units of the third decimal C.G.S.; the maximum correction is about 15 units for either chart. For the greater part, both charts give, in general, too high values.

The observations received from the present cruise down to Porto Rico, which are already in my office, and the cable dispatch received from Mr. Peters, in command of the "Carnegie," when he arrived at the mouth of the Amazon on September 24, prove that the results of the first cruise are being borne out by the present one. The "Carnegie" left Para on the fifteenth instant to continue her journey down the South American coast as far as Buenos Aires; from thence she will cross to Cape Town, arriving there towards the end of March, 1911, where the speaker expects to join her.

B. *Atmospheric Electricity.*—Observations for specific conductivity of the atmosphere, with a Gerdien conductivity apparatus, and the detection of the presence of radio-active emanations, using an apparatus of the Elster and Geitel type, were taken on the "Carnegie" by Mr. Edward Kidson on the portions of the cruise between Falmouth and Madeira, Madeira and Bermuda, and Bermuda and New York. The plan was to devote alternate days to conductivity and radio-activity observations. This program was

interfered with by bad weather and by the failure on some occasions of the Zamboni dry pile which was used to charge the collecting wire in the radio-activity experiments.

From the observations obtained, no connection could be established between atmospheric pressure, humidity, wind, or cloud and the conductivity. When, however, there was a visible fog or haze the conductivity was greatly reduced. Rain squalls of short duration did not produce any effect. As the conductivity is an extremely variable quantity, a very large number of observations is required before the connection with meteorological conditions can be thoroughly investigated. One effect that was noticed was that a low conductivity was invariably obtained when the vessel was in the neighborhood of land. This effect was heightened in Long Island Sound on the vessel's return in winter by the state of the atmosphere then prevailing and probably by the presence of snow on the land and ice on some stretches of water.

Another noticeable fact was the persistent excess of the positive conductivity over the negative. The only occasions on which the reverse appeared to be consistently the case were while the ship was at anchor off Madeira and in Hamilton harbor, Bermuda. This higher value of the positive conductivity is probably due chiefly to the accumulation of positive ions near the negatively charged earth's surface. If this were so, then the effect should not be so noticeable in balloon observations as believed to be the case.

None of the present theories seem sufficient to explain the high degree of ionization observed in the air.

On December 18–19 continuous observations of the conductivity were taken over practically twenty-four hours, in order to discover, if possible, a diurnal variation. The day was exceedingly calm and fine, with a glassy sea with a smooth, low swell. The results point to a higher value of the conductivity at night than during the day, and to an almost constant value at night. This latter effect is more obvious if the individual observations be all plotted, when the variations are seen to be much greater and more irregular during the day time. It would be interesting to secure more of these continuous observations.

The chief results of the observations for the detection of radio-active matter in the atmosphere are as follows: The evidence thus far gathered points to the absence of any considerable quantity of thorium emanation in the air over the ocean; however, more observations are needed to decide the question definitely. On several days, when the vessel was very far from land, very little activity was collected; particularly was this the case on December 11, 14 and 18. The region in which this happened was a very calm one, and the air had probably not been in contact with the land for many days. Mr. Kidson is inclined to think, therefore, that the land is the chief source of the radio-active matter in sea air. This is what would be expected from deter-

minations of the radium content of sea water. The fact that Mr. P. H. Dike, the observer on the "Galilee" in the Pacific, could obtain no evidence of radio-activity except near land, also points to this conclusion. The Pacific Ocean being of so much greater extent than the Atlantic, there should be much larger tracts over which the air had lost any radio-activity got from the land. The absence of thorium emanation would tend to confirm this theory.

It is easy to understand that the air in the North Atlantic between Newfoundland and England may at times have all been over land surfaces within a week. This may account for the results obtained by Professor Eve in this region.[1] Observations comparing the amounts of radio-activity over land and ocean are much needed.

[Just as this abstract is passing through the press I am enabled to quote from Mr. Kidson's report on his most recent observations as follows:

"On the cruise between San Juan and Para observations for conductivity were obtained on twelve days and for radio-activity on seven days. On August 29–30, 1910, a continuous series of conductivity observations were taken over practically twenty-four hours with the assistance of Messrs. Frary and Carroll. The results of this series do not appear to confirm those of last year, but on the 29th the conductivity was higher than I had ever observed it before. On the following day it fell to a lower value than it had had during the night. The same variability was shown. On the whole, the high values of the conductivity have been obtained. The amount of radio-active matter collected has been small. On two days a small quantity of sea water was evaporated and the residue tested for radio-activity while on another day a little rain water was tested in the same way. In neither case could any activity be detected."]

C. *Atmospheric Refraction Observations.*—These observations consisted in the determination of the "dip of the horizon," being made for the purpose of controlling the corrections to be applied to the astronomical observations on account of atmospheric refraction. The observer was J. P. Ault, the navigating officer on the first cruise, Pulfrich's dip measurer, made by Zeiss, being used, in which by the aid of prisms, the two horizons to the right and to the left are seen as two parallel vertical lines in the field of view of the small telescope, the distance apart of the lines being equal to twice the angular value of the dip of the horizon, read off in minutes by means of a scale.

The corrections found on the values obtained from atmospheric refraction tables were, in general, negative, reaching a maximum of $-1'.02$, showing the tabular value to be too large; however, on the portion of the cruise between Bermuda and New York the corrections in the mean are positive, the maximum being $+1'.23$. The dip of the horizon being a correction which is applied directly to an observed altitude of a celestial body, if then in case the latitude is obtained from meridian altitude it would be in error by the same amount as the dip correction, hence in the maximum $1\frac{1}{4}$ of a minute of arc

[1] A. S. Eve, Terr. Mag., v. 15, 1909, 25.

or of a nautical mile, or nearly 1½ statute miles. The error in longitude will vary from one minute to over three minutes of arc, allowing a celestial body an azimuth of over thirty-five degrees from the meridian and for a range in latitude from twenty degrees north to fifty degrees north; for extreme conditions the error may even be greater.

It is thus seen that it is highly desirable for the mariner to have accurate tables of atmospheric refraction, especially near land, where an error of a mile or two in the ship's position is a matter of grave importance. In fact our attention to the need of such observations was first called by mariners themselves, who have found at various times when nearing the coast, where the opportunity was afforded to check their astronomical positions by land objects, that their positions were out presumably due to the tabular values of atmospheric refraction. How far the atmospheric refraction tables may depend upon prevailing meteorological conditions must be left for future examinations when additional data are at hand.

D. *Gravity Observations.*—Suggestions have been received from various sources that it would be highly desirable to include, if possible, gravity work on the "Carnegie." In 1905 I consulted Professor Helmert, Director of the Geodetic Institute at Potsdam, as to the possibility of attempting such work on the "Galilee," which at the time was chartered, as may be recalled, for the magnetic work in the Pacific Ocean. One of his assistants, Dr. Hecker, had employed the method of getting gravity results at sea by determining the temperature of the boiling point of water, deducing therefrom the corresponding atmospheric pressure and comparing this with the observed mercurial barometric height referred to normal gravity, the outstanding difference being the measure of the gravity anomalies within the inevitable observational errors. He had made a cruise on a passenger steamer in 1901 from Hamburg to Rio de Janeiro and back to Lisbon ; again in 1904 he made further cruises in the Indian and Pacific Oceans and in 1909 also in the Black Sea. As the result of Hecker's experiences, Professor Helmert did not think it possible to get anything of value on such a small vessel as the "Galilee," and we accordingly made no attempt.

However, on the "Carnegie," it was decided to make as frequently as possible determinations of the temperature of the boiling point of water with the prime view of obtaining the data required for controlling the corrections of our aneroids. The instrumental equipment was in accordance with this chief purpose, and hence only two boiling point apparatuses, furnished each with a thermometer, and an ordinary Green marine mercurial barometer, were provided. In all one hundred and two determinations were made, representing seventy-five different points, four of which were the ports Brooklyn, Falmouth, Madeira and Bermuda. It should be said that the observer, Dr. C. C. Craft, had no idea of the possible use of his results for gravity; however, a very searching examination has convinced me that with

the necessary refinement in instrumental equipment and in method of observation it will be possible to obtain gravity results on the "Carnegie" worth while. While the results on the first cruise cannot be used for determining the gravity anomaly over any restricted area, a general deduction can be drawn, in view of the large number of observations and the varying conditions under which they were made, which harmonizes with the general conclusion of Hecker's work, namely, that gravity is in general normal over the deep oceans, the defect in the density of the aqueous material above the ocean bottom being made up very nearly by increased density of the material below the ocean bottom. If we average our results then the mean anomaly over the deep part of the Atlantic Ocean, three to seven kilometers, differs from the mean over the shallow part along the coasts, five to two hundred meters, by about +0.04 of a dyne, meaning that there is a slight defect in gravitational force over the deep ocean by that amount as compared with the force over shallow water. This is to be regarded merely as a provisional result, the probable error being of about same amount as the quantity itself; it is, however, in the same direction as Hecker's conclusions, he getting figures on the order of +0.02 to +0.055 of a dyne. A difference of .035 of a dyne corresponds approximately to an error of 0.001 of a degree in the temperature of the boiling point of water. The average difference in the temperatures of the boiling point for the two thermometers used and for a single determination was 0.006 of a degree, the average result above depends upon 75 stations. In his latest work Hecker employed 9 specially constructed mercurial barometers and six thermometers and six boiling point apparatuses.

In connection with this investigation I have had occasion to examine into the various tables for obtaining the atmospheric pressure corresponding to the temperature of the boiling point of water, the latest of these tables in general use being those of Wiebe's given in Landolt-Börnstein's Physikalisch-Chemische Tabellen. The most recent observations appear to be those of Holborn and Henning. For the purpose of gravity work, it is essential to be able to obtain accurately the atmospheric pressure for a comparatively limited range extending below and above 100° C.; the observations on which the tables are based were made at larger intervals, and the interpolation is accordingly somewhat uncertain. It is quite possible that the atmospheric pressure as taken from the tables may be out .05 to 0.1 mm. which corresponds to 0.065 to 0.135 of a degree in gravity. When dealing with only differential results of gravity, as we are in the present instance, the tabular errors are somewhat eliminated, though not wholly. I desire to bring this problem of more accurate vapor tension tables for water between 99° and 101° C. to the attention of physicists.

Attention is now to be given to a careful study of the various sources of error and their relative quantitative effects with the view of introducing the necessary refinements in the future work from the standpoint of observation as well as of computation.